

Effective Charge Transfer and Covalent Bonding in III-V Compounds

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Difference in electron charge transfer from the two kinds of atoms in III-V compounds to the bond is equivalent to effective charge transfer from one kind of atom to the other, resulting in a net dipole moment. The conclusion that the charge transfer to the bond is proportional to the effective charge transfer is supported by analysis of the Mössbauer, thermal conductivity and elasticity data. In an analysis of the short-range force parameters, the central force parameter α is charge-independent whereas the noncentral force parameter β is highly correlated with the effective charge transfer. Further, α is correlated with $C_0 = e^2/r^4$ whereas β is not. The quite different correlations observed for α and β suggest that other physical properties be reexamined for relation to central and noncentral force effects. The apparent shift of the centroid of the bonding charge towards the V atom is due to the larger transfer of charge from the V atom to the bond. The role of the relative occupation of valence states must be accounted for in the comparison of physical properties for the different groups of semiconductors.

Introduction

The purpose of this paper is to deduce the nature of the chemical bond in III-V semiconducting compounds from the evidence of the experimental data. The present study is limited to the III-V family of compounds since experimental data are most abundant for this group, and further, in order to eliminate from consideration those factors which may depend upon the occupation of the valence states.

Three significant aspects of the crystal bond in III-V compounds are the magnitude of the effective charge transfer, the polarity of this charge transfer, and the electron density in the bond. Direct and indirect evidence of these characteristics is the subject of this paper.

Direct experimental evidence for the direction of the effective charge transfer in III-V compounds is found in the results of Fourier synthesis of the electron density from X ray data (1, 2); static piezoelectric measurements (3, 4); dynamic piezoelectric measurements (5); and Mössbauer isomer shift measurements (6). In these measurements, the experimental results indicate an effective electron charge transfer from the V atom to the III atom in a systematic pattern (7).

Correlation between the effective charges obtained by optical methods and charges deduced by Fourier synthesis of the charge density from X ray data has been demonstrated (2, 7), if the difference in polarizability of the atoms is taken into account.

A direct correlation between the effective covalent charge transfer and the reduced microhardness has been demonstrated (7). Comparison between the experimental electron and hole mobilities, and theoretical mobilities based on polar mode scattering has also been obtained (1, 2).

Piezoelectric measurements have been utilized to determine the sign and magnitude of the charge transfer in semiconductor compounds. Typical techniques are the static method of Zerbst and Boroffka (3) and the dynamic method of Arlt and Quadflieg (5). Zerbst and Boroffka evaluated the charge transfer in GaAs to be $-0.51 e$, that is, from the As atom to the Ga atom. Hambleton (4), using similar techniques, came to the same conclusion. Arlt and Quadflieg did not report a true charge, instead they evaluated a term that is a function of the charge. They conclude that the charge transfer in III-V

compounds is negative, electronic charge is transferred from the V atom to the III atom. Comparison and correlation of these piezoelectric measurements with the evaluation of charge transfer obtained by Fourier synthesis of the charge density has been made, where the authors deduced that, at least for III-V compounds, electronic polarizability does not have a large effect in piezoelectric measurements, whereas it does in optical measurements. These piezoelectric measurements are further considered in a latter section below.

Further correlations between charge transfer and other physical properties such as band gap energies, electron effective mass, and spin-orbit splitting energies have been demonstrated (7). A pattern of effective charge transfer has been deduced in which charge transfer and other physical properties are found to be functions of $Z(V) + 2.5 Z(III)$ (7).

Review of Recent Work

I. Mössbauer Data

In Fig. 1, the effective covalent charge transfer is compared with the Mössbauer isomer shift for ^{121}Sb in InSb, GaSb, and AlSb (6). The covalent charges were determined from the Fourier synthesis of the X ray data for InSb (1) and for GaSb (2). The charge for AlSb was estimated from empirically derived relationships between the charges and physical properties of III-V compounds (7). The results of the Mössbauer isomer shift measurements indicate a shift of

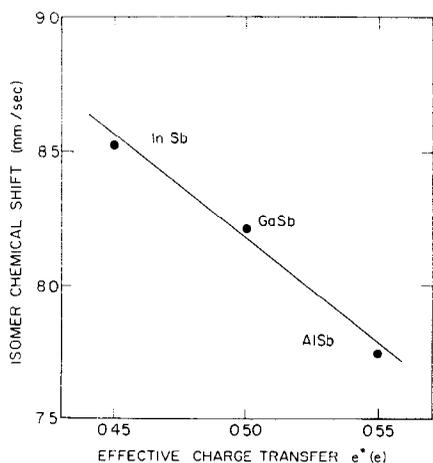


FIG. 1. Mössbauer isomer chemical shift (6) as a function of effective charge transfer (1, 2, 7). The signs of the x and y variables are both negative.

electron charge away from the Sb atom with increasing magnitude in the series InSb, GaSb, AlSb (6), with the implication that the charge is transferred to the III atom (6). Hence, conclusions about the direction of effective charge transfer are supported by an independent measurement. Further, deductions about the magnitude of the effective charge transfer for AlSb, which were obtained from empirical relations (7), are reinforced. Interpretation of these data is considered in a section below.

II. Thermal Conductivity Data

In a recent publication on lattice thermal conductivity in semiconductors, Spitzer (8) states that the lattice thermal conductivity should decrease with increasing ionicity. This conclusion is in part based upon the theories of Ioffe and Ioffe and Suchet, as discussed by Spitzer (8). In Fig. 2, the lattice thermal conductivity for III-V compounds is compared with the effective charge transfer. We note that the data fall into two

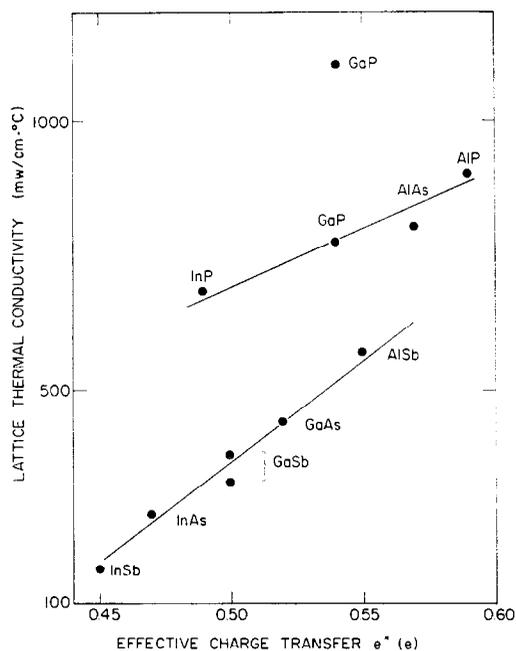


FIG. 2. Lattice thermal conductivity (8) as a function of effective charge transfer (1, 2, 7). The pair of values for lattice thermal conductivity for GaP are as given in Spitzer's paper (8). The large discrepancy may be due to off-stoichiometric composition of one or both of the samples used in the respective measurements. In comparison with LTC of the III-V compounds as a group, the lower value is considered to be the more representative for GaP. See also Fig. 3 regarding this point.

groups, and that each group of data points exhibit the same trend; there is an increase in lattice thermal conductivity with an increase in effective charge transfer. This observation is not in conflict with the statement mentioned above, since we must distinguish between "ionic" and "covalent" charges in III-V compounds.

III. Elastic Properties

In the ionic case, the charges on the atoms are localized at the atomic sites, with negligible electron density between the atoms. Such an ionic compound will have bond-stretching restoring forces, but would not have bond-bending restoring forces for small deformations. In the covalent case, there is considerable electron density in the bonds, and these bonds are highly directional. Covalent compounds would therefore have appreciable bond-bending restoring forces in addition to bond-stretching restoring forces.

In the valence force field model of Musgrave and Pople (9), the elastic properties of crystals are related to bond-bending and bond-stretching restoring forces. In this model, for the sphalerite structure, the shear coefficients C_{44} and $(C_{11} - C_{12})/2$ should be independent of central forces through second nearest neighbors, whereas the bulk modulus $(C_{11} + 2C_{12})/3$ should depend only upon central forces. In this model, shear elastic moduli should decrease to the vanishing point as the ionic charge increases and the bond charge density decreases (10).

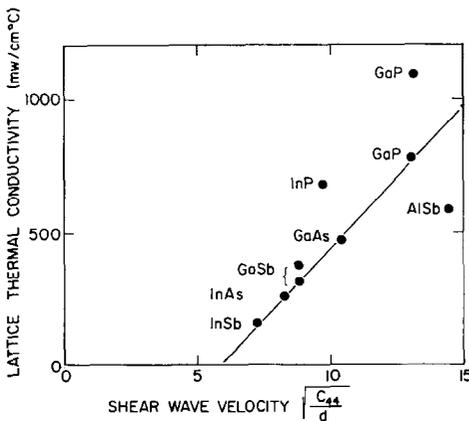


FIG. 3. Lattice thermal conductivity (δ) as a function of shear wave velocity. Note that the smaller of the two values of thermal conductivity for GaP is consistent with the remainder of the data, whereas the larger value is not representative. See Fig. 2 regarding this point.

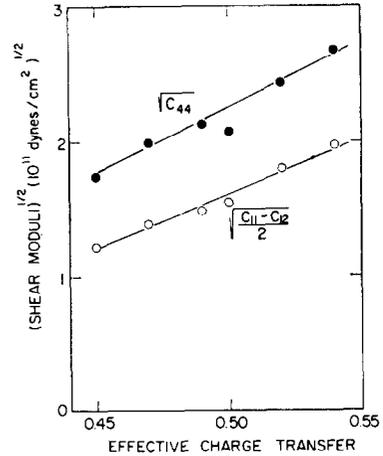


FIG. 4. Square root of shear moduli (10) as a function of effective charge transfer on III-V compounds (1, 2, 7).

The lattice thermal conductivity is proportional to the velocity of elastic waves in the crystal. For longitudinal waves along the cube axis the velocity is $(C_{11}/d)^{1/2}$, where d is the density. The velocity of shear waves along the cube axis is $(C_{44}/d)^{1/2}$. In Fig. 3, the lattice thermal conductivity is shown as a function of the shear wave velocity.

In Fig. 4, the shear elastic moduli are compared with the covalent charge transfer for III-V compounds. The data indicate that the shear moduli increase with the effective charge transfer, being larger for large transfer of charge.

The short-range force parameters, which were calculated from the elastic moduli data by Martin (10), show significant correlations. The central force parameter α was found to be

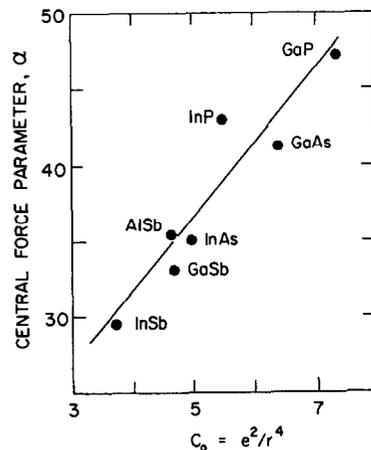


FIG. 5. The short-range central force parameter as a function of C_0 .

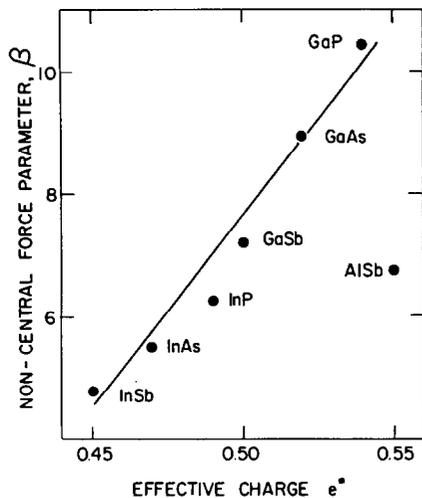


FIG. 6. The short-range noncentral force parameter as a function of the effective charge transfer.

correlatable with the elastic term $C_0 = e^2/r^4$ (Fig. 5), where r is the interatomic distance, and e is the electronic charge, but not with the effective charge transfer. The noncentral force parameter β , on the other hand, was found to be correlatable with the effective charge transfer (Fig. 6) but not with C_0 . The central force parameter is charge-independent while the noncentral force parameter is highly charge-dependent in that β changes by over a factor of two for a change of 20% in the effective charge transfer. The quite different correlations observed for central and noncentral forces suggest that other physical properties be reexamined for relation to central and noncentral force effects. For example, we may infer that lattice thermal conductivity is dependent upon noncentral forces to a greater degree than it is dependent upon central forces, although effect of both is evident (Fig. 2).

Discussion

Elastic Properties

The correlations observed between effective charge transfer and elastic properties support the assumption that charge transfer to the bond is proportional to the effective charge transfer from one atomic species to the other in III-V compounds.

Martin (10) has obtained reduced elastic moduli by dividing the experimental moduli by the factor $C_0 = e^2/r^4$, where r is the interatomic distance and e is the electronic charge. Martin's reduced elastic data appear to support the

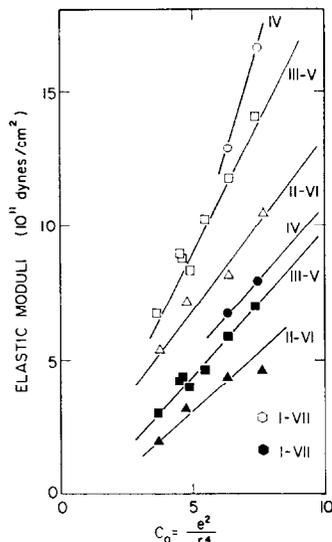


FIG. 7. Elastic moduli as a function of C_0 (10). The values for carbon are not shown due to the scale factor. The carbon points do fall on the corresponding lines for the IV elements. The open symbols are the C_{11} elastic moduli; and the solid symbols are the C_{44} elastic moduli.

assumption that shear and bulk moduli decrease as the ionicity [based on the dielectric model of Phillips and VanVechten (11-14)] increases. However, the apparent decrease with dielectric ionicity is due to the grouping of the data into IV, III-V, II-VI, and I-VII regions which are relatively constant. In Fig. 7, some elastic moduli are shown as a function of C_0 . The separation of the data into groups is indicated, as well as the constancy of the slope for each group. The elastic moduli are proportional to C_0 , the proportionality factor is constant for each group but differs from one group to the other. This separation may be due to the difference in occupation of the valence states for each group, which may have a larger effect than differences in ionicity. This effect is shown in Fig. 8 where the slopes of the elasticity data in Fig. 7 are given as a function of the semiconductor group and the difference in the number of valence electrons for neutral atoms, which is a measure of the relative occupation of valence states.

Bond Charge Relations

Proper analysis of chemical bonding requires that the charge transfer be considered in terms of three entities, the III atom, the V atom, and the bond. In this situation, charge may transfer from one atom to the other, or charge may

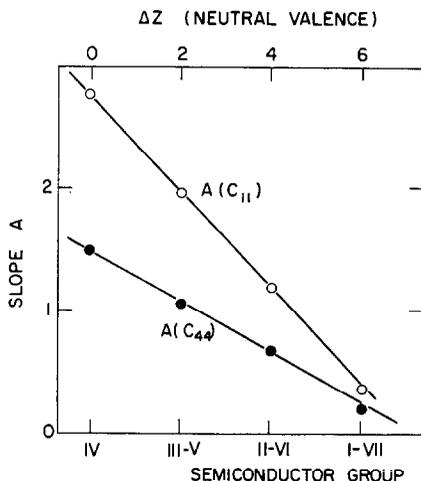


FIG. 8. The slopes of the elastic moduli data in Fig. 7 as a function of semiconductor group and the difference in valence electrons for neutral atoms. The slopes for the groups, IV, III-V, and II-VI were obtained by least-mean-square fitting of the data to the equation

$$C_{JJ} = A(C_{JJ}) C_0 + B.$$

The value of slope A for the I-VII group was estimated by assuming zero intercept since data for only one compound was given in Ref. (10).

transfer from the two kinds of atoms to the bond by different amounts. In the first instance, the charge would be negative on the III atom and positive on the V atom. In the second instance the charges on both atoms would be positive although the difference in the magnitudes of the charges on the atoms may be the same as in the first instance. Experiments which yield results that are sensitive to the difference in the charges on the two atoms would not be capable of distinguishing between these two cases.

We now derive some simple relationships between the charges involved in the charge transfer models.

Let

$Q(\text{III})$ be the actual charge on the III atom;
 $Z(\text{III})$ be that atomic number of the III atom;
 $q(\text{III})$ be the charge transferred from the III atom to the bond;

$q(\text{V})$ be the charge transferred from the V atom to the bond;

s be the charge transferred from the III atom to the V atom;

e^* be the effective charge transfer from the III atom to the V atom;

ΔQ be the valence charge difference between the V atom and the III atom;

B Total charge per bond;

p difference between charge transferred from the V atom to the bond and charge transferred from the III atom to the bond; $p = q(\text{V}) - q(\text{III})$.

We have used the usual convention for s and e^* where each is negative in the instance that charge is transferred from the V atom to the III atom for the corresponding term. We obtain the following relationships:

$$Q(\text{V}) = Z(\text{V}) - [q(\text{V}) - s] \\ = Z(\text{V}) + e^*$$

$$Q(\text{III}) = Z(\text{III}) - [q(\text{III}) + s] \\ = Z(\text{III}) - e^*$$

$$\Delta Q = Q(\text{V}) - Z(\text{V}) - Q(\text{III}) + Z(\text{III}) \\ = 2e^* \\ = 2s - p$$

$$B = \frac{q(\text{V}) + q(\text{III})}{4}.$$

Let $n = q(\text{III}) + s$.

Let $n - \Delta Q = q(\text{V}) - s$.

We note that the bonding charge B is therefore dependent only upon n and ΔQ for any suitable combination of p , q , s . Further for the case s is zero, we obtain

$$-2e^* = p.$$

The ΔQ may be evaluated from piezoelectric measurements or from X ray data where the relative intensities are obtained by scaling to the theoretical scattering factors of neutral atoms (1, 2).

The $q(\text{V})$ or $q(\text{III})$ may be evaluated from Mössbauer isomer shift measurements which are sensitive to s electron density, NQR measurements which are sensitive to p electron density, absorption edge measurements which are sensitive to total electron density in the vicinity of the individual atoms, or, in fact, any method which can determine the electron density at one atomic species without regard to conditions at the other atomic species.

Interpretation of Measurements

In the comparison of measurements for interpretation of the energy shifts for the elements in various compounds and in the elemental state, we should appreciate the fact that the atoms in the elemental solid state need not be "neutral," where an appreciable degree of covalency is

present. Hence, a remaining charge on an atom in the elemental state does not necessarily imply "ionic bonding" in the same sense in which the term is generally used. Hence discretion must be utilized in the comparison of energy shifts for atoms in elements and in related compounds. This is particularly true in the case where the relative shifts for the two kinds of atoms in III-V compounds are obtained by comparison with the pure elemental forms of the same constituents, since the two individual elemental forms need not possess the same degree of neutrality or covalency. Where feasible, measurements of the solid elements should be compared with similar measurements on the gaseous phase, in order that firmer conclusions of the absolute degree of covalency can be deduced.

Estimation of the Bond Charge

In Ref. (6), a theoretical isomer shift of -11 mm/sec per s electron is given, with a p -electron shielding of ± 1.7 mm/sec at the $5s^1p^3$ configuration. We now assume that the isomer shift is the weighted average value obtained for the case of complete hybridization. We obtain either

$$-\frac{1}{4}(11) + \frac{3}{4}(1.7) \text{ mm/sec per electron} = -1.475 \text{ mm/sec per electron for the } p\text{-shielding case, and}$$

$$-\frac{1}{4}(11) - \frac{3}{4}(1.7) \text{ mm/sec per electron} = -4.025 \text{ mm/sec per electron for the anti-shielding case.}$$

We assume the p -shielding case for the calculations in Table I.

$$b = \text{number of valence electrons on the Sb atom}$$

$$= -\frac{\text{ICS}}{1.475} + C$$

ICS = Mössbauer isomer chemical shift

C = constant

$q(V)$ = charge transferred from the Sb atom

$q(\text{III})$ = charge transferred from the III atom

$$= q(V) - p$$

$$p = 2e^*$$

B = total electronic charge per bond

$$= \frac{q(\text{III}) + q(V)}{4}$$

The value of the constant C had to be determined separately since the isomer shift was determined relative to the source SnO_2 . The estimate of C was obtained from the assumption that the charge

TABLE I
CALCULATION OF THE BONDING CHARGE FROM MÖSSBAUER MEASUREMENTS (6)

	InSb	GaSb	AlSb
ICS	-8.52	-8.21	-7.75
b	$5.78 + C$	$5.57 + C$	$5.25 + C$
$q(V)$	$-0.78 - C$	$-0.57 - C$	$-0.25 - C$
e^*	-0.45	-0.50	-0.55
p	0.90	1.00	1.10
$q(\text{III})$	$-1.68 - C$	$-1.57 - C$	$-1.35 - C$
C	-3.026	-3.066	-3.004
$q(V)$	2.26	2.47	2.78
$q(\text{III})$	1.36	1.47	1.68
B	0.90	0.98	1.11

transferred from each atom is proportional to the initial occupation of valence states:

$$\frac{q(V)}{q(\text{III})} = \frac{5}{3}$$

We note that the value of C obtained for these three compounds is within 1% of the average value of -3.032 . A corresponding result is not obtained for the anti-shielding case. The values of $q(V)$, $q(\text{III})$ and the bonding charge B are given in the last three rows of Table I, using the average value of $C = -3.032$. The following results are obtained:

1. The charge transferred from the Sb atom, $q(V)$ increases in the series InSb, GaSb, AlSb.

2. The charge transferred from the III atom, $q(\text{III})$, increases in the same series.

3. The bond charge B also increases in the same series.

4. The bond charge B and the effective charge e^* are both approximately one-half of the value expected in the case where all of the valence charge is transferred to the bond.

5. The ionic charges on the two kinds of atoms in III-V compounds are not equal in magnitude nor opposite in sign. Both kinds of atoms are positively charged, by different amounts. Calculations based upon assumed charges of $+Q$ and $-Q$ on the two kinds of atoms require re-examination. In general, the above relations may be written as:

$$q(\text{III}) = X - C - p$$

$$q(V) = X - C$$

$$R = q(V)/q(\text{III})$$

$$X = 5 - \text{ICS}/\text{ICS}_{\text{th}}$$

$$p = -2e^*$$

Whence:

$$\begin{aligned} C &= X - pR/(R - 1) \\ q(\text{III}) &= p/(R - 1) \\ q(\text{V}) &= pR/(R - 1) \\ B &= p(R + 1)/4(R - 1) \end{aligned}$$

We note that the bonding charge B depends only upon the effective charge transfer e^* and the ratio of charge transfer R . We note further that in order for C to be consistent for a series of compounds, all three quantities X , p , R must be simultaneously appropriate for all the materials considered. Hence, since the deviation of C is about 1% from the average value, the assumption of p -shielding in the calculation of the theoretical ICS_{th} and the charge ratio $R = 5/3$ are justified. For this value of R ,

$$\begin{aligned} q(\text{III}) &= 3p/2, \\ q(\text{V}) &= 5p/2, \\ B &= p. \end{aligned}$$

Centroid of the Bonding Charge

We must consider the interpretation of the apparent shift of the centroid of the bonding charge from the midpoint of the bond towards the V atom. In one example, Walter and Cohen (15) have calculated electron density and covalent bonding charge for several diamond and zincblende semiconductors using wavefunctions derived from pseudopotential band-structure calculations. They observe that the charge density is concentrated halfway between the two atoms for Ge; and further, that in the case of GaAs, the center of the bonding charge has moved towards the As ion. Doggett (16), using bond orbital wave functions and multicenter integral approximations, has calculated the electronic charge distribution in BN. Doggett observed an appreciable accumulation of charge density about the N atom which is distinctly polarized in the direction of the bond in the total electron density map. This is true for both neutral B^0N^0 and B^-N^+ . Doggett also prepared difference electron density maps in which the density function for neutral B and N, situated at their perspective lattice sites, were subtracted from the crystal density function, where each N and B atom was given a hybrid orbital occupation of $5/4$ and $3/4$, respectively. In this difference electron density map, while charge is lost from the vicinity of both the N and B nuclei, it is accumulated in the center of each bond, and not

in a region closer to the N atom than the B atom. This observation is valid for the two cases considered, B^0N^0 and B^-N^+ .

We deduce that the shift of the centroid of the bonding charge toward the V atom does not indicate a net shift of charge towards that atom, but may indeed indicate the opposite case, a predominantly greater shift of charge from the V atom to the bond.

Suppose, for example, in an extreme case that the III atom does not contribute electronic charge to the bond but that the V atom does contribute. We would therefore expect the centroid of the electronic charge in the bond to be much closer to the V atom than to the III atom. In the case that both kinds of atoms contribute electronic charge to the bond, the centroid of the bond charge will be closer to the atom that contributes the most charge. The charge in the bond appears to be displaced toward the V atom whereas there is actually a larger shift of charge away from the V atom than from the III atom. In effect, the apparent shift of the centroid of the bond charge is towards the larger *source* of the bond charge.

In the case of silicon carbide, the existence of a crystal dipole moment is clearly explainable if the two kinds of atoms contribute unequally to the bond. The observed dipole is not explainable, however, if only charge transfer between the two kinds of atoms is considered.

Piezoelectric Effects

Several possible mechanisms for the origin of the piezoelectric effect have been discussed by Arlt and Quadflieg (5), including ionic polarization, change in ionicity, and electronic polarization. Phillips and Van Vechten (17) have endeavored to explain the change in sign of the piezoelectric effect in going from II-VI to III-V compounds (5). They assert that the sign of the piezoelectric term e_{pol} is determined by whether ionic polarization or change in ionicity is the dominant factor. Further comparison of the core-and-shell models with the charges-and-dipoles models is discussed by Kobl and Tolpygo (18) who develop an adiabatic theory of lattice vibrations.

The comparison of the results of different types of measurements leads to interesting conclusions. As stated previously (2, 7), correlation between optical effective charges and X ray effective charges has been demonstrated if the difference in polarizability of the atoms is taken

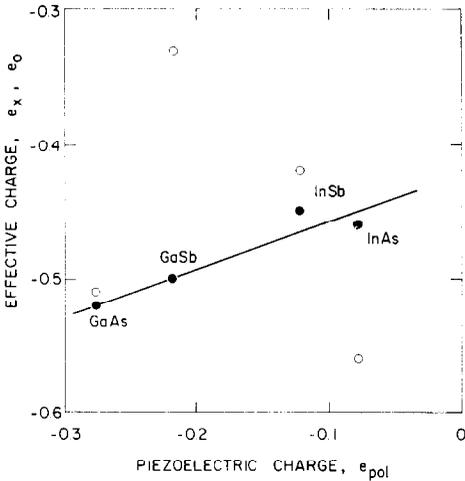


FIG. 9. The X ray effective charge e_x (1, 2) (●) as a function of the piezoelectric charge $e_{pol} = 3(e_{14})^{1/2}$. On the same scale, the optical effective charge e_0 (19) (○) are shown for comparison.

into account. Comparisons between these effective charges of Arlt and Quadflieg (5) has been previously discussed (2) and are indicated in Fig. 9 where the closed circles are the X ray effective charges and the open circles are the optical effective charges. The following observations are to be noted:

1. The linear correlations between the X ray effective charges e_x and the piezoelectric charges $e_{pol} = \sqrt{3}e_{14}$ is significant, whereas similar correlation between the optical effective charges e_0 and e_{pol} is lacking. In due consideration of the relation between e_0 and e_x discussed above, Attard et al. (2) deduced that, at least for III-V compounds, electronic polarization does not have a large effect in piezoelectric measurements, whereas it does in optical measurements.

2. The linear correlation between e_x and e_{pol} in Fig. 9 further demonstrates that e_{pol} can change sign, for the same type of compound, even if the effective charge e_x does not change sign.

This latter observation then forces us to reconsider the significance of the reverse in sign of the piezoelectric effect in going from III-V to II-VI compounds. In Fig. 10 the noncentral force parameter β of III-V and II-VI compounds is compared with the piezoelectric charge e_{pol} . The data for the II-VI compounds is seen as an extension of the data for III-V compounds, showing the same general trend. This situation is not the case when the central force parameter

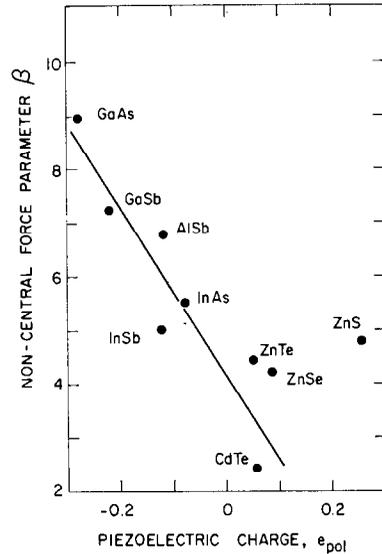


FIG. 10. The short-range noncentral force parameter (β) as a function of e_{pol} (5).

α is compared with e_{pol} . Sufficient information is not available at present to clarify the mechanism of the piezoelectric effect, which appears to be more complicated than previously suspected.

Conclusions

1. Difference in electron charge transfer from the two kinds of atoms in a diatomic lattice to the bond is equivalent to charge transfer from one kind of atom to the other, resulting in a net dipole moment.

2. Experimental methods which are sensitive to the difference in the charges in the two atoms are not capable of discriminating between the two cases. Appropriate methods are those which can determine energy shifts or electron density on the different kinds of atom sites directly without regard to corresponding conditions at the other atomic species. Alternately, methods which can determine the bond charge directly are clearly appropriate for this investigation.

3. In the case of III-V compounds, electron charge is transferred from both the III atom and the V atom to the bond, with the V atom contributing more charge than the III atom.

4. The amount of charge transferred to the bond is proportional to the effective charge transfer from one atomic species to the other.

5. The centroid of the bonding charge is apparently shifted towards the V atom as a result of the larger transfer of charge to the bond.

6. The short-range central force parameter α is charge-independent whereas the short-range noncentral force parameter β is highly correlated with the effective charge transfer. α is correlated with the elastic parameter $C_0 = e^2/r^4$ while β is not. The quite different correlations for α and β suggest that other physical properties be re-examined for similar relations for central and noncentral effects.

7. The role of the relative occupation of valence state must be accounted for in the comparison of the relative physical properties for different groups of semiconductors, as, for example, in comparison of the physical properties of III-V and II-VI compounds and IV elements.

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