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Piezoelectricity in III–V Compounds with a Phenomenological Analysis of the Piezoelectric Effect

By

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The piezoelectric stress constants e_{14} of InSb, InAs, GaSb, GaAs, and AlSb have been measured at room temperature and found to be 0.071; 0.045; 0.13; 0.16, and 0.068 C/m^2 respectively. If the III–V compound crystals are expanded in the $\langle 111 \rangle$ direction, the A-faces (metal atoms) become negatively charged, in contrast to II–VI compounds, in which the equivalent faces become positively charged. Using a model of a layered lattice, we show that three different mechanisms may contribute to the piezoelectric effect. These mechanisms are 1. the internal displacement of the ionic charge, 2. the internal displacement of the electronic charge. 3. the change in ionicity due to strain.

Die piezoelektrischen Konstanten e_{14} von InSb, InAs, GaSb, GaAs und AlSb wurden bei Raumtemperatur bestimmt. Sie sind in der gleichen Reihenfolge 0,071; 0,045; 0,13; 0,16 und 0,068 C/m^2. Dehnt man eine III-V Verbindung in $\langle 111 \rangle$ Richtung, so laden sich die A-Flächen (begrenzt durch Metallatome) negativ auf, im Gegensatz zu II–VI Verbindungen, in denen äquivalente Flächen positiv werden. An einem linearen Gittermodell wird demonstriert, daß drei verschiedene Mechanismen zum piezoelektrischen Effekt beitragen können: innere Verrückung von Ionen, innere Verrückung von Elektronen und Änderung der Ionizität.

1. Introduction

In a recent paper [1] we have described a new method, which allows the measurement of the piezoelectric stress constant e_{14} of semiconductors of fairly high conductivity, i.e. those semiconductors in which the piezoelectric polarization is effectively screened off by free carriers. We report here some results on III–V compounds which are interesting with respect to their magnitude and sign. We show on a simplified lattice model (linear chain) that the internal displacement of the ions is not the only mechanism causing piezoelectric effects. The different mechanisms are partly inherent in the lattice theories of Birman [2], and Tolpygo [3] and Merten [4].

2. Measuring Method

The experimental set-up for the piezoelectric Hall effect measurement is shown in Fig. 1. A rod of fused silica, 4 cm in length, with a 5 MHz x-cut quartz transducer bonded to one face and two strips of the III–V compound under investigation bonded to the other face, is excited to a longitudinal resonance vibration near 5 MHz, containing many half wavelengths. The two strips have a thickness of half a wavelength of the ultrasound and are oriented so that the outer face of one is the (111) plane, and that of the other is the $(\bar{1}\bar{1}\bar{1})$ plane. They are electrically connected as shown.

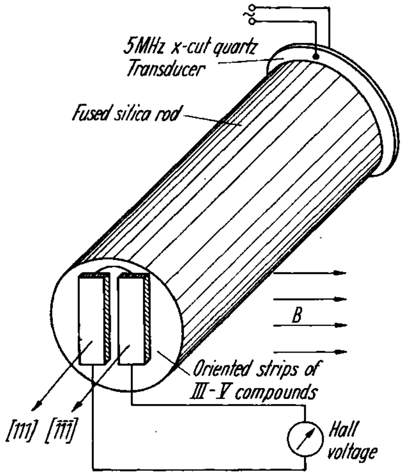

Fig. 1. Arrangement for measuring the piezoelectric Hall effect

The ultrasonic vibration generates an electric current in the strips in the ⟨111⟩ direction which transports the charge necessary to compensate the piezoelectric polarization. We apply a magnetic field **B** perpendicular to the current and to the length of the strips and get a Hall voltage V_H between the ends of the strips. The derivation of this voltage gives [1] for $\omega \tau_\varepsilon \ll 1$

$$V_H = -j\,\omega\, l\, R_H\, B\, \frac{2}{\pi}\, S\, \frac{2}{\sqrt{3}}\, e_{14}\,, \qquad (1)$$

where τ_ε is the dielectric relaxation time, ω the angular frequency of the sound, l the total length of the two strips, R_H the Hall coefficient, B the magnetic field strength, $\frac{2}{\pi} S$ the average strain amplitude in the strips, and $\frac{2}{\sqrt{3}} e_{14}$ the piezoelectric constant of sphalerite type crystals in the ⟨111⟩ direction.

The Hall coefficient R_H was determined by conventional methods. To measure the strain amplitude S, an insulating SiO layer was evaporated on to the strips, which was then covered with thin evaporated silver strips. During vibration in the magnetic field a Lorentz force voltage is induced in the silver strips, which is proportional to their velocity, i.e. to the velocity of the surface of the III–V compound. From the Lorentz force voltage the strain amplitude can be calculated [5]. Lorentz force voltages induced in the III–V compound strips can be neglected because of two peculiarities of the arrangement: (i) The strips have a thickness of half a wavelength, thus having no average velocity component. (ii) Due to the series connection of the two strips (shown in Fig. 1) piezoelectric Hall voltages add, whereas Lorentz force voltages cancel.

Phase and amplitude of the voltages were measured, allowing a phase comparison between the piezoelectric Hall voltage in the III–V compound and the Lorentz force voltage in the thin silver layers. From this comparison the sign of the piezoelectric effect was deduced.

3. Experimental Results

Table 1 shows the results of our measurements. The coupling coefficients $K_{TS\langle 110\rangle}$ for thickness shear waves propagating in a ⟨110⟩ direction, and those for thickness extensional waves along a ⟨111⟩ direction, $K_{TE\langle 111\rangle}$, were calculated using the measured piezoelectric constants e_{14}, the low-frequency dielectric constants ε_r and the elastic constants as given in textbooks [6].

The estimated accuracy of the piezoelectric constants e_{14} results from the precision with which the different factors in equation (1) were determined. Measurements were carried out on at least four different samples of each of the investigated III–V compounds, cut from different single crystals often of different

Table 1

Piezoelectric properties of III-V compounds at room temperature

A-B	e_{14} (C/m^2)	Estimated accuracy $\pm$	Polarity*)	Coupling constants $K_{TS}\langle 110\rangle$	$K_{TE}\langle 111\rangle$	ε_r
InSb	0.071	10%	−	3.3×10^{-2}	2.27×10^{-2}	17
InAs	0.045	20%	−	2.0×10^{-2}	1.38×10^{-2}	14.5
GaSb	0.126	20%	−	5.3×10^{-2}	3.7×10^{-2}	15
GaAs	0.16	10%	−	6.2×10^{-2}	4.5×10^{-2}	12.5
AlSb	0.068	20%	−	3.3×10^{-2}	2.3×10^{-2}	11.5

*) Sign of the piezoelectric polarization charge on the A-side, if the crystal is expanded in the $\langle 111\rangle$ direction.

Table 2

Complete set of piezoelectric constants of III-V compounds at room temperature

A-B	e_{14} (C/m^2)	d_{14} (m/V)	g_{14} (m^2/C)	h_{14} (V/m)
InSb	0.071	2.35×10^{-12}	1.57×10^{-2}	4.7×10^{8}
InAs	0.045	1.14×10^{-12}	0.89×10^{-2}	3.5×10^{8}
GaSb	0.126	2.9×10^{-12}	2.2×10^{-2}	9.5×10^{8}
GaAs	0.16	2.7×10^{-12}	2.4×10^{-2}	14.5×10^{8}
AlSb	0.068	1.64×10^{-12}	1.61×10^{-2}	6.7×10^{8}

origin. The spread in the measured constants was somewhat smaller than the estimated accuracy.

Table 2 presents the piezoelectric constants d_{14}, g_{14}, and h_{14} as derived from the measured e_{14}. On high-ohmic GaAs several conventional measurements have been reported, e.g. by Charlson and Mott [7] who found $d_{14} = 2.6\times10^{-12}$ m/V, and Hambledon [8] who found $d_{14} = 2.63\times10^{-12}$ m/V. These are in good agreement with our results. Somewhat lower are the values reported by White [9] who found $e_{14} = 0.12$ C/m^2 and by Zerbst and Boroffka [10] who measured $g_{14} = 1.37\times10^{-2}$ m^2/C The sign of the piezo electric effect in GaAs as determined by Zerbst and Boroffka [10] and by Hambledon [8] is the same as that found by us in all III–V compounds.

The A-faces of the III–V crystals, defined as those {111} faces composed of the metal atoms, were determined by common etching techniques [11].

In Table 3 the piezoelectric constants of some II–VI compounds as given by Berlincourt et al. [12], crystallizing in the same cubic sphalerite structure as the III–V compounds, are given for comparison with Table 1. With the exception of ZnS the effects are weaker in II–VI than in III–V compounds. However, the polarity of the piezoelectric effect in II–VI compounds, as measured, is opposite to that in III–V compounds. ¹)

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¹) We have confirmed the sign of the piezoelectric constant e_{33} in CdS as given by Berlincourt et al. [12] by applying our measuring technique to low ohmic CdS.

Table 3

Piezoelectric constants of sphalerite type II-VI compounds [12]

A-B	CdTe	ZnTe	ZnSe	ZnS
e_{14} (C/m^2) Polarity*)	0.031 ?	0.0284 +	0.049 ?	0.147 +

*) See subscript to Table 1.

Table 4

Piezoelectric constants of cubic and hexagonal compounds

Cubic		Cubic		Hexagonal	
A-B	$\sqrt{3}\, e_{14}$ (C/m^2)	A-B	$\sqrt{3}\, e_{14}$ (C/m^2)	A-B	e_{33} (C/m^2)
InSb	−0.123	CdTe [12]	0.054	CdSe [12]	+0.35
InAs	−0.078	ZnSe [12]	+0.049	CdS [12]	+0.44
GaSb	−0.218	ZnSe [12]	0.085	ZnS*)	+0.27
GaAs	−0.277	ZnS [12]	+0.254	ZnO [17]	+1.10
AlSb	−0.118			BeO [17]	0.092

*) Derived from A. I. Morozov et al. [18] on the assumption $d_{31} = -\frac{1}{2} d_{33}$ and the elastic constants given by C. F. Cline et al. [19].

The crystal structure of cubic ZnS is closely related to the hexagonal structure of wurtzite-type crystals, as discussed in many textbooks and also, with respect to piezoelectricity, in the paper by Berlincourt et al. [12]. In both structures we can find polar directions along which the crystal consists of alternating layers of metal atoms A and nonmetal atoms B with spacing ratio 1:3 (in hexagonal crystals only approximately valid). In hexagonal crystals there is only one such polar axis, i.e. along the c-direction. In cubic crystals, however, there are four polar axes along the four $\langle 111 \rangle$ directions, giving no average polar behaviour. This has to be considered when a comparison of the piezoelectric effect between sphalerite-type and wurtzite-type crystals is made.

A longitudinal strain S along the polar c-axis in hexagonal crystals causes the dielectric displacement vector to be $D_3 = e_{33} S_3$ (under constant electric field) where e_{33} is the piezoelectric constant. If, however, a cubic ZnS-type crystal is longitudinally strained along the [111] direction then we expect to get contributions to the dielectric displacement vector in this direction not only from this polar axis but also from the other three polar directions, i.e. $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$, because there is also a strain component in these directions. Calling that contribution to the total effect which is due to the [111] polar axis e_{pol}, we can derive from geometrical arguments that the total dielectric displacement is $D_{\langle 111 \rangle} = \frac{2}{3} e_{\text{pol}} S_{\text{long}\,\langle 111 \rangle}$. Thus e_{pol} is a piezoelectric quantity comparable with e_{33} in hexagonal crystals. From tensor analysis it follows that $D_{\langle 111\rangle} = \frac{2}{\sqrt{3}} e_{14} S_{\mathrm{long}\langle 111\rangle}$, thus $e_{\mathrm{pol}} = \sqrt{3}\, e_{14}$. In Table 4 the values of e_{pol} for cubic crystals are compared with the values of e_{33} for hexagonal crystals. The sign attributed to the piezoelectric constants is defined in the subscript of Table 1.

The strength of the piezoelectric properties of the III–V compounds is between that of the cubic II–VI compounds and that of the strongly piezoelectric hexagonal II–VI compounds. It is worth noting that the piezoelectric constants of cubic ZnS and hexagonal ZnS, although derived with an assumption (see subscript of Table 4), are roughly equal. The most outstanding effect is the change in sign, in the transition from III–V to II–VI compounds. If the piezoelectric effect is interpreted in terms of internal displacement of ions this would result in negatively charged metal atoms in III–V compounds, and positively charged metal atoms in II–VI compounds. With a simple lattice model, however, we will show that the interpretation of the piezoelectric effect resting exclusively on internal displacements of ionic charges is quite unsatisfactory.

4. Origin of Piezoelectric Effects

The left-hand side of Fig. 2 shows alternating layers of atoms A and B with spacings a and b. It represents the one-dimensional model of a layered lattice with polar axis z and having a lattice constant $l = a + b$. In the middle part of Fig. 2, the charge distribution in the lattice along z is displayed schematically. It is separated into the *positive* charge of the atomic *cores* and the negative electronic charge distribution. With boundaries $\beta_{\mathrm{A}}^{\mathrm{B}}$ and $\beta_{\mathrm{B}}^{\mathrm{A}}$ between the layers (dashed lines) one can uniquely define an ionicity of the model, which is the total charge Q_{A} or Q_{B} respectively between two adjacent boundaries. On the right-hand side of Fig. 2, the continuous electronic charge distribution along z is replaced by discrete charges q'_{A} and q'_{B} representing the total *electronic* charge between two adjacent boundaries located at its centre of charge. This centre need not be identical with the loci of the positive charges q_{A} and q_{B} of the cores. The ionicity of the two layers A and B is thus $Q_{\mathrm{A}} = q_{\mathrm{A}} + q'_{\mathrm{A}}$ and $Q_{\mathrm{B}} = q_{\mathrm{B}} + q'_{\mathrm{B}}$, and because of neutrality $Q_{\mathrm{A}} = -Q_{\mathrm{B}}$.

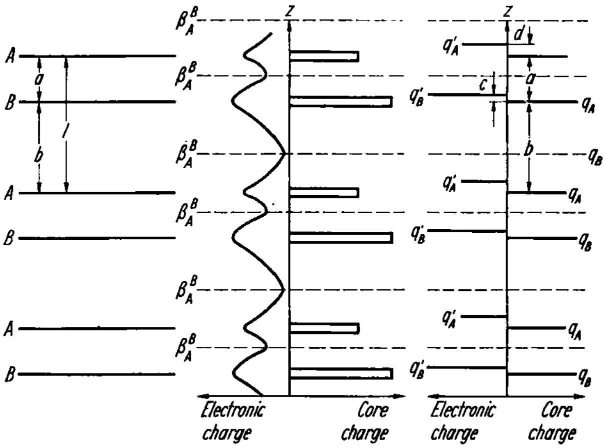

Fig. 2. Charge distribution in a linear lattice model consisting of alternating atom layers A and B

For a number n of double layers, we calculate the polarization vector $\boldsymbol{P}$ along z:

$$P = \sum_i q_i z_i = n\,(a\,Q_A + c\,q'_B + d\,q'_A)\,. \tag{2}$$

If we now apply a longitudinal strain $S = \partial l/l$ in the z-direction, the polarization vector $\boldsymbol{P}$ changes, causing a piezoelectric effect. The piezoelectric constant e_{pol} of this model is defined as the change of the dielectric displacement D with applied strain S, under constant electric field strength (which is realized in an experiment by the high conductivity or by short-circuited electrodes on the end faces):

$$e_{\text{pol}} = \frac{\partial D}{\partial S} = l\,\frac{\partial D}{\partial l} = l\,\frac{\partial\left(\frac{P}{n\,l}\right)}{\partial l}\,. \tag{3}$$

If we introduce relative internal displacements Γ_s, defined by $\Gamma_s = \left(\frac{\partial s}{\partial l} - \frac{s}{l}\right)$ with $s = a$, c, or d, we find, after inserting (2) in (3), and after differentiation, the different terms describing the origin of the piezoelectric effect:

$$e_{\text{pol}} = Q_A\,\Gamma_a + q'_A\,\Gamma_d + q'_B\,\Gamma_c + \frac{\partial Q_A}{\partial l}\,(a + d - c)\,. \tag{4}$$

The first term of equation (4) represents the internal displacement of *ionic* charges. It is widely used for the interpretation of the piezoelectric effect. The next two terms are internal displacements of *electronic* charges relative to the core, i.e. the electronic polarization of the ionic layers. The fourth term describes the piezoelectric contribution due to the strain-induced change in ionicity or, in other words, to the charge transfer from the space between one pair of boundaries to the space between the neighbouring boundaries.

The charge transfer, however, is only allowed over one boundary, say β_B^A. Difficulties at the real crystal boundaries over which no transfer of polarization charge is possible would arise if we were to allow a flow of polarization charge over both boundaries.[2])

Apart from the above we have not yet given any detailed conditions for the position of the boundaries β_A^B and β_B^A either in the unstrained or in the strained crystal. As soon as we postulate a geometrical condition for the boundaries in the unstrained crystal, we define an ionicity which, however, does not necessarily conform with one of the many other definitions of the ionicity. If we accept one of the existing definitions of the ionicity, then it is in principle possible to position our boundaries in conformity with that definition.

Furthermore we have not yet fixed a condition for the displacement of one boundary, say β_B^A when the crystal is strained. If we can apply one of the existing definitions of the ionicity also to the strained crystal, then we can again displace β_B^A in conformity with it. In this case we would get contributions to the piezoelectric effect from all three mechanisms: ionic and electronic displacement and change of ionicity. As mentioned above, the displacement of the other boundary is fixed by the condition that no charge flows over it.

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[2]) This condition is necessary to get an unique solution for the piezoelectric constant e_{pol}. It makes e_{pol} independent of the choice of the zero-point of the z-axis and independent of the choice of the crystal boundaries. It expresses the fact that polarization charge is bound to the crystal and cannot flow in or out over its real boundaries.

If, however, no definition of the ionicity in the *strained* lattice exists, in displacing $\beta_{\mathrm{B}}^{\mathrm{A}}$ we can define it e.g. in one or two ways either there is no charge transfer over it, or the total electronic polarization $q'_{\mathrm{A}}\,\Gamma_a + q'_{\mathrm{B}}\,\Gamma_c$ is zero. In the first case, which is accepted in many theoretical papers, it is assumed that the ionicity is not changed by the strain; in the second case it is assumed that the electronic polarization does not vary if the crystal is strained.

The above considerations show that the distribution of the total piezoelectric effect between the different terms in equation (4) depends largely on the definition of the ionicity in the unstrained and the strained lattice. We see, however, that whatever may be the definition of ionicity, it is not sufficient to describe piezoelectricity only by internal displacement of ions.

We can compare the origin of the piezoelectric effect with that of the dielectric polarization, where we are quite familiar with the fact that the *electric* polarizability can usually be separated into three parts: ionic, electronic, and orientational. The above model shows that *mechanical* polarizability can be separated into the ionic part, the electronic part, and the change in ionicity. If we had chosen a somewhat more complex model, including molecules having a permanent electric dipole moment, we would have found a further contribution to the piezoelectric constant due to the mechanically induced reorientation of the molecular dipoles.

No experimental methods exist yet to distinguish the various contributions to the piezoelectric effect. Simple approximations and measurements, however, show that all three mechanisms can give contributions of the same order of magnitude, not necessarily all of the same sign:

1. *Ionic polarization*

If we assume every A-atom in a zincblende or in a wurtzite-type crystal singly positively charged and the internal displacement to be of the order [13] $\Gamma_a \approx 0.5$ we get an ionic contribution

$$\Gamma_a\, Q_{\mathrm{A}} = \frac{\sqrt{3}}{8}\,\frac{e^2}{b^2} \approx -0.6\,\frac{\mathrm{C}}{\mathrm{m}^2}\,,$$

where e is the electronic charge, b the next-nearest neighbour distance, and $\frac{\sqrt{3}}{4\,b^2}$ the number of atoms per unit area in the layers A or B of our model. The numerical value is calculated with $b = 2.5$ Å.

2. *Change in ionicity*

Assuming the singly positively charged atoms A to lose all their charge linearily in expanding the lattice, such that if $\partial l \approx l$ (which is clearly not realizable) all atoms would become neutral, we have $\frac{\partial Q_{\mathrm{A}}}{\partial l} = \frac{\sqrt{3}}{4}\,\frac{e}{b^2}$. Since $l = \frac{4}{3}\,b$ and $(a + d - c) \approx 1/4\,b$ we get

$$(a + d - c)\,\frac{\partial Q_{\mathrm{A}}}{\partial l} = -\,\frac{\sqrt{3}\,e}{16\,b^2} \approx +0.3\,\frac{\mathrm{C}}{\mathrm{m}^2}$$

again taking $b = 2.5$ Å.

3. *Electronic polarization*

We do not know any realistic approximation for the electronic polarization due to mechanical strain. Therefore we mention here the measured piezoelectric effect of Te [14] and Se [15]. In these crystals the total piezoelectric effect has to be ascribed to the electronic polarization, because it is not reasonable to assume ionic charges on the Te or Se atoms in the trigonal crystals. If we apply an equivalent model to the above for the trigonal Te, we calculate from our measurements on Te [16] a piezoelectric constant $e_{\text{pol}} = \frac{4}{3} e_{11}$ (i.e. the value which is reduced to one polar axis):

$$|e_{\text{pol}}| = |\Gamma_a q'_{\text{A}} + \Gamma_c q'_{\text{B}}| \approx 0.55 \frac{\text{C}}{\text{m}^2}.$$

The above considerations give evidence that the rigid ion model will fail in most cases if used as the theoretical basis of piezoelectricity. It has to be replaced by a model which includes electronic polarization and strain-induced change of ionicity. Further work is necessary to show whether the shell model, which has had remarkable success in the interpretation of dielectric behaviour, or any other model which takes account of electronic polarization and change in ionicity will give consistent results if applied to piezoelectric properties. Numerical results of the different contributions, however, have no meaning, as long as the ionic charge per atom is not a well defined quantity.

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