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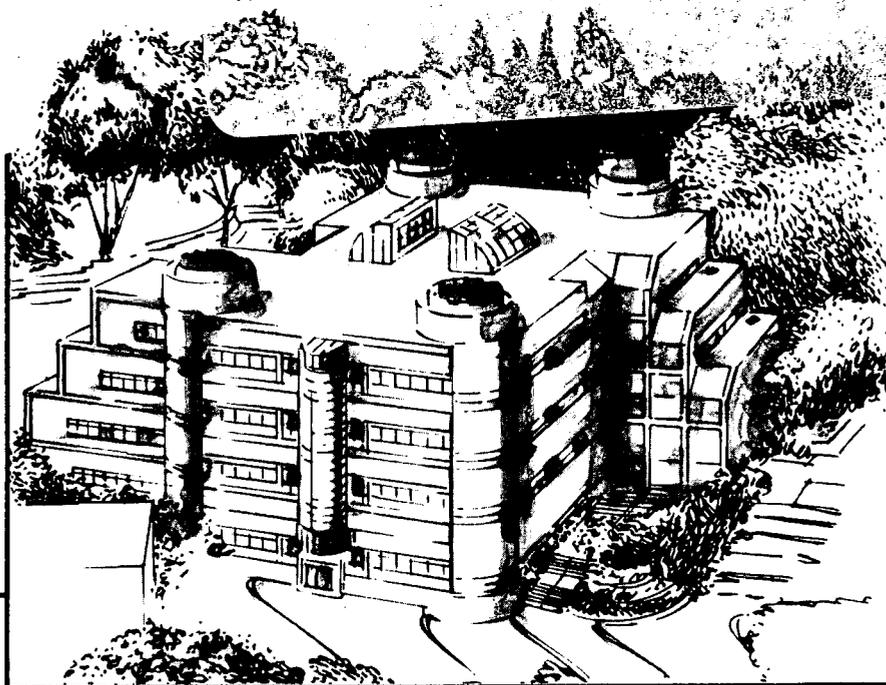
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Band-Edge Hydrostatic Deformation Potentials in III-V Semiconductors

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Abstract:

We report experimental values for the band-edge hydrostatic deformation potentials of GaAs and InP semiconductors. The deformation potentials are determined directly by observing the universal pressure derivative of transition metal defect levels and considering this pressure derivative in the context of recent models of heterojunction band line-up. We obtain values of -9.3 eV and -7.0 eV for the conduction band deformation potentials of GaAs and InP respectively, determined from uniaxial stress deep level transient spectroscopy on defect levels of Ti and V.

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In this Letter, we present the first direct experimental values for the band-edge hydrostatic deformation potentials of GaAs and InP measured with respect to transition metal defect levels. These transition metal deep levels have recently been proposed to provide stable reference levels from which bulk and interface properties can be measured^{1,2}. While the theory of deformation potential scattering of charge carriers in semiconductors has a long history³ and enjoys a relatively advanced understanding, the magnitudes of the electron-phonon coupling parameters have been a source of debate for several decades⁴⁻⁶. The net change in the bandgap under pressure can be measured easily⁷, but the independent hydrostatic shifts of the conduction and valence band edges have heretofore eluded direct measurement.

In the previous absence of direct measurement, attempts had been made to calculate the deformation potentials theoretically from first principles^{8,9}, or to extrapolate the deformation potentials indirectly from mobility or free carrier absorption data^{5,8,10,11}. These attempts led to a wide scatter of values. Experimentally, the effect of acoustic phonon deformation potential scattering is often barely distinguishable from the effects of other scattering mechanisms, and mobility or free carrier absorption data can be fit for wide ranges of values of the deformation potential. The direct method we propose allows for the measurement of band-edge deformation potentials with an accuracy considerably better than current indirect methods. Our approach is based on the equivalence between strain-induced band discontinuities and the band discontinuities at heterojunction (HJ) interfaces. The topic of HJ band offsets has received extensive interest lately because of its technological implications in bandgap engineering, and a strong theoretical and empirical foundation has been laid to explain and predict band discontinuities. In particular, the deep energy levels of transition metal defects have been used as a means of

predicting band line-up².

It has been noted both experimentally^{2,12}, and theoretically¹ that the relative energy separations among the transition metal defect levels remain essentially constant within a family of isovalent semiconductors. This striking invariance led to the suggestion² that a common bulk reference energy level exists for these defects. It was proposed that the same reference level could be used to explain the heterojunction band alignment between two isovalent compounds. Experimental evidence from the lattice-matched GaAs-AlAs system tended to corroborate this conjecture. This apparent line-up of transition metal energy levels across an interface between two isovalent semiconductors can be justified by comparing calculations of transition metal defect energies¹³ with theories of band-edge line-up across a heterojunction interface^{9,14,15}. The defect levels in the gap are non-bonding levels which have energies that are bounded by the energies of the maximum-density of states in the valence and conduction bands. These same valence and conduction band energies determine the so-called charge-neutrality^{14,15} energy which is assumed to match up across a semiconductor interface. The non-bonding nature of the transition metal levels relate the defect energies intimately with the neutrality level. A more rigorous treatment of this relationship¹⁶ predicts that the transition metal defect levels are "locked" to the neutrality level to within an additive constant.

If the neutrality level lines up across a hetero-semiconductor interface, the transition metal energy levels are forced to line-up across the same interface. This principle is quite general and is insensitive to the details of how the band structures of the two semiconductors differ. For example in the presence of strain inhomogeneity, such as in a phonon field, a strain-induced homojunction occurs. Such a homojunction is shown schematically in Fig. 1.

The band offsets at the interface are directly proportional to the band-edge deformation potentials. In order to measure the deformation potentials, a strain-induced homojunction is not explicitly required. The transition metal defect levels are locked to the neutrality level, and therefore provide internal reference levels from which changes in the band-edge can be measured. By measuring the pressure derivative of the transition metal defects, one is in fact measuring the pressure derivative of the band-edge of the bulk material. Implicit in our argument is the prediction that the transition metals should possess a "universal" pressure derivative in a given material, independent of chemical species or charge states. This expectation is partially corroborated by theoretical calculations¹⁷ that predict that Ga-site T_2 states have essentially the same pressure derivatives regardless of the energy separation from the band-edge. We now provide experimental verification of this universal pressure derivative.

To measure the deformation potentials in InP and GaAs, we have applied uniaxial stress in conjunction with deep level transient spectroscopy (DLTS) to the $3+/2+$ transitions¹⁸ of Ti and V in GaAs, and the $3+/4+$ transitions of Ti in InP and GaAs. These levels are shown in Fig. 2. Shear contributions to the transition metal energy shifts are at most 5 meV/GPa for stress in $\langle 100 \rangle$ directions¹⁹, and smaller or zero for stress in $\langle 111 \rangle$ directions. Therefore the shift in the transition metal DLTS energies for $\langle 111 \rangle$ stress arises almost entirely from the hydrostatic component of the uniaxial stress. The energy shifts of Ti and V in n-GaAs as a function of stress are presented in Fig. 3. The pressure derivatives of $Ti(3+/2+)$ and $V(3+/2+)$ are found to be equal to within experimental error ($\approx 10\%$), and have a deformation potential of $a_c = -9.3 \text{ eV} \pm 1 \text{ eV}$. The $Ti(4+/3+)$ level in LEC n-GaAs produces a DLTS peak on the high temperature (430 Kelvin) flank of the EL2 signal. The pressure derivative of this

defect yields $a_c = -7 \pm 2$ eV for the conduction band minimum. The larger error associated with this measurement is caused by the interference from the EL2 signal. In addition to our data on Ti and V in GaAs, results for Cr(2+/1+) and Cr(3+/2+) in GaAs²⁰ are also available. The results of GaAs:Cr are of special significance because these transitions involve changes in the occupancy of the t_2 levels in the d-shell compared to the Ti(3+/2+) and Ti(4+/3+) transitions which involve only changes in e-state occupancy. The pressure derivative of the Cr(3+/2+) acceptor level was measured with respect to the conduction band to yield a deformation potential of -7.0 eV. The pressure derivative of the Cr(2+/1+) level, normally degenerate with the conduction band, was also found to be -7.0 eV. Both of the pressure derivatives of Cr in GaAs were obtained through fitting broad luminescence peaks with gaussian lineshapes. This technique is expected to produce errors larger than the errors arising in DLTS. The deformation potentials in GaAs determined through the three chemical species Ti, V and Cr among the four different charge states 1+, 2+, 3+ and 4+ are therefore all equal within 30%.

Considering only the more accurate results from the 3+/2+ levels in GaAs, we find a deformation potential $a_c = -9.3$ eV \pm 1 eV for the bottom of the conduction band. By considering the bandgap deformation potential⁷ of 8.6 eV, this gives the top of the valence band a deformation potential of $a_v = -0.7$ eV \pm 1 eV. We obtain a value of $a_c = -7$ eV \pm 1 eV for the conduction band of InP based on the measurement of the Ti(4+/3+) donor level in n-type InP. The valence band deformation potential of InP is obtained to be $a_v = -0.6$ eV through subtraction of the band-gap deformation potential²¹ of 6.4 eV from the conduction band value.

The existing experimental values of the deformation potentials determined from the analyses of carrier transport or free carrier absorption are

highly unreliable as they range from -7 eV to -17.5 eV in GaAs^{4,5} and from -3.4 eV to -18 eV in InP^{10,11}. Such large variations of a_c lead to more than one order of magnitude spread in the relative contribution of deformation potential scattering to the total scattering rate. The high values of the deformation potentials were in most cases obtained from fitting of the electron mobility⁵ or free carrier absorption⁸ to theoretical models in which the effect of compensation was not accounted for. It has been shown recently⁶ that the best fit to electron mobility in high-purity, low-compensation GaAs is obtained with a_c in the range -9 eV to -10 eV. Our direct measurement of a_c is in excellent agreement with this result.

The introduction of AlGaAs/GaAs modulation doped heterostructures allowed for a substantial reduction of ionized impurity scattering, enhancing the relative contribution of acoustic phonons in limiting the low temperature electron mobility. However, even in this case the values of the deformation potential used to explain the temperature dependence of the electron mobility^{22,23} ranged from -7.0 eV to -13.5 eV. Lately, there is growing evidence based on new mobility calculations²⁴ that the value of $a_c = -8.5$ eV satisfactorily accounts for the acoustic phonon deformation potential contribution to the electron scattering in n-GaAs/AlGaAs heterostructures. In addition, an analysis of the hole mobility in p-type GaAs/AlGaAs modulation doped heterostructures provided a value²⁵ of $a_v = -1.0$ eV again in excellent agreement with our present determination.

Much less data is available for the deformation potentials of InP. The present determination of -7 eV is consistent with the values^{26,27} $a_c = -6.5$ eV and -6.8 eV to explain electron mobility. Evidently, our measurements cannot be reconciled with such large values¹¹ as -18 eV or such small values¹⁰ as -3.4 eV for the conduction band deformation potential reported in the literature.

The acoustic phonon scattering of the valence band holes can be described in terms of the effective deformation potential

$$\Xi_{\text{eff}}^2 = a_v^2 + (c_l/c_t)[b_v^2 + (1/2)d_v^2]$$

where a_v , b_v , d_v are valence band deformation potentials and c_l and c_t are longitudinal and transverse elastic constants. The constants b_v and d_v are well known from uniaxial stress experiments²⁸. Using our values of a_v , we obtain $\Xi_{\text{eff}}(\text{GaAs}) = 6.1$ eV and $\Xi_{\text{eff}}(\text{InP}) = 6.6$ eV which compare very favorably with the values 6.6 eV and 7.0 eV reported in Ref.28.

It is evident from the above discussion that our values of the hydrostatic deformation potentials can explain consistently experimental data on electron and hole mobility in GaAs and InP. This provides additional support for the proposed method of directly measuring the band-edge deformation potentials using the transition metal defect levels. We note finally that the present experimental data confirm the most recent theoretical calculations which report values⁹ of $a_c(\text{GaAs}) = -8.8$ eV and $a_c(\text{InP}) = -5.9$ eV. Our results also agree with calculations that predict that a_v is typically an order of magnitude smaller than a_c ²⁹. In conclusion, we have shown, for the case of GaAs, that different transition metal species among different charge states possess a universal pressure derivative. We propose that this pressure derivative is in fact the pressure derivative of the band-edge of the bulk material. The corresponding values for the band-edge deformation potentials are much more accurate than those determined by indirect methods, and give a consistent explanation of a variety of experimental data on electron and hole mobility in GaAs and InP. This technique is simple, and universal, and should be applicable to both III-V and II-VI semiconductors.

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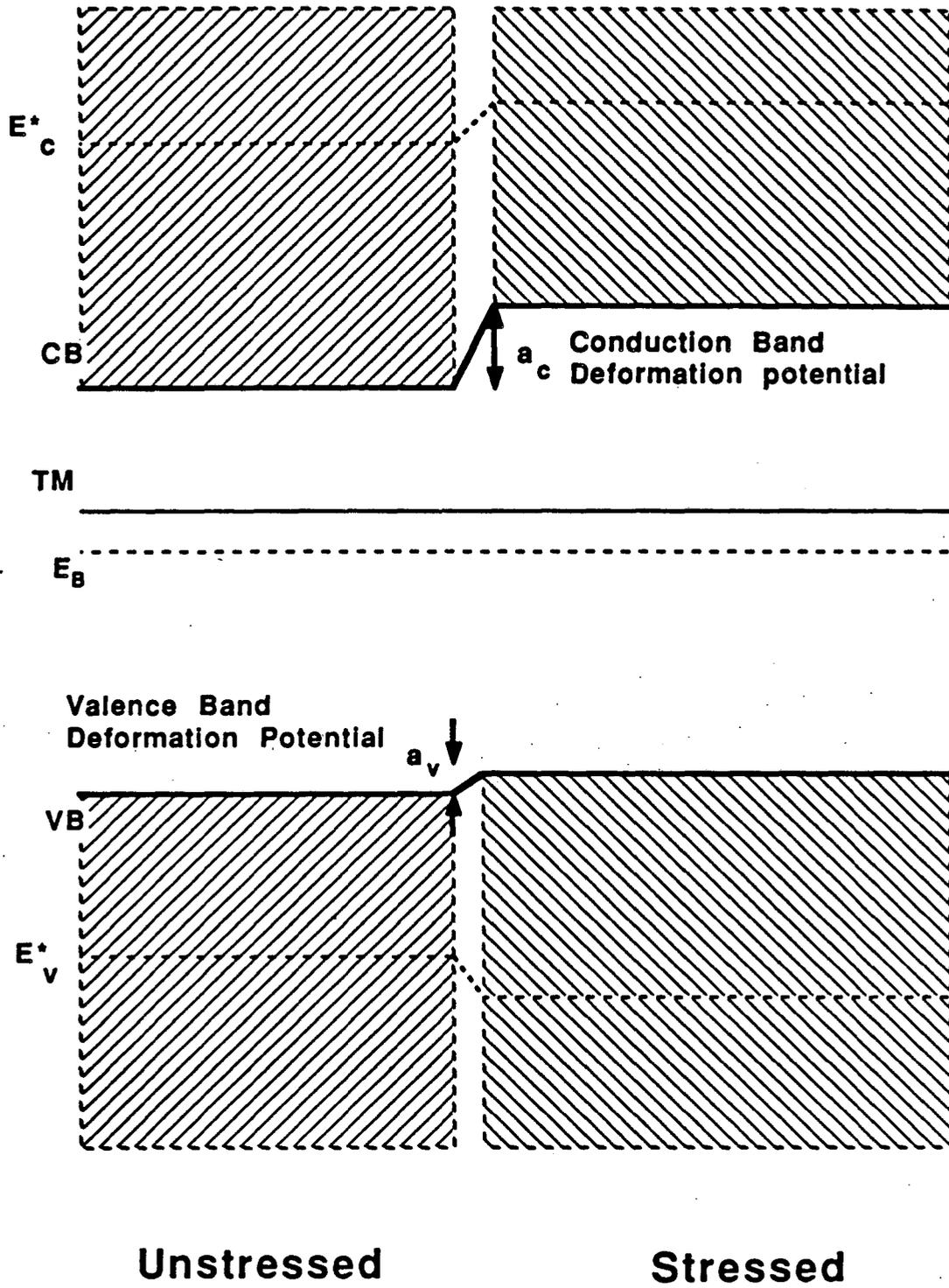
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Figures:

- 1) **Strain-induced homojunction.** The semiconductors on the left and right differ only by their state of strain. The neutrality level E_B and the transition metal (TM) level are both dominated by the energies in the conduction band and valence band with the maximum density of states, denoted by E_C^* and E_V^* respectively. The band discontinuity caused by the strain inhomogeneity is directly proportional to the band-edge deformation potential.

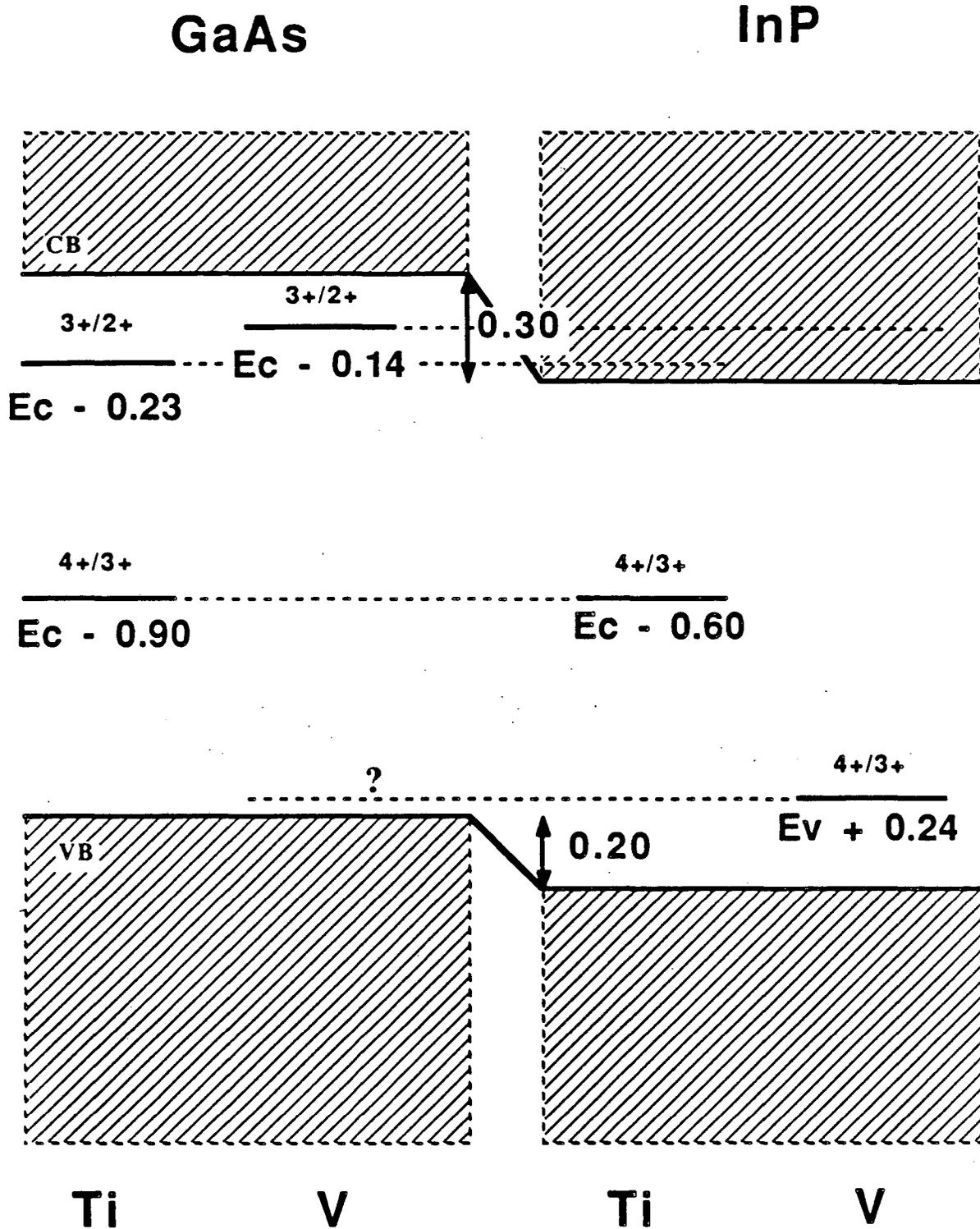
- 2) **Energy positions of the (3+/2+) and (4+/3+) levels of Ti and V** substitutional impurities in GaAs and InP. The band offset is adjusted to line up the Ti(4+/3+) level between the materials. The V(4+/3+) level in GaAs is not observed and is assumed to lie within the valence band.

- 3) **Energy shifts of DLTS peaks as a function of <111> oriented uniaxial stress for two chemical species (Ti, V) among three charge states (2+, 3+, 4+) in GaAs.** The corresponding deformation potential for the band-edge of GaAs is $a_c = -9.3 \pm 1$ eV. These data, with previous data for Cr(2+/1+) and Cr(3+/2+)²⁰, provide evidence for the universal pressure derivative of the transition metals (within 30 %).



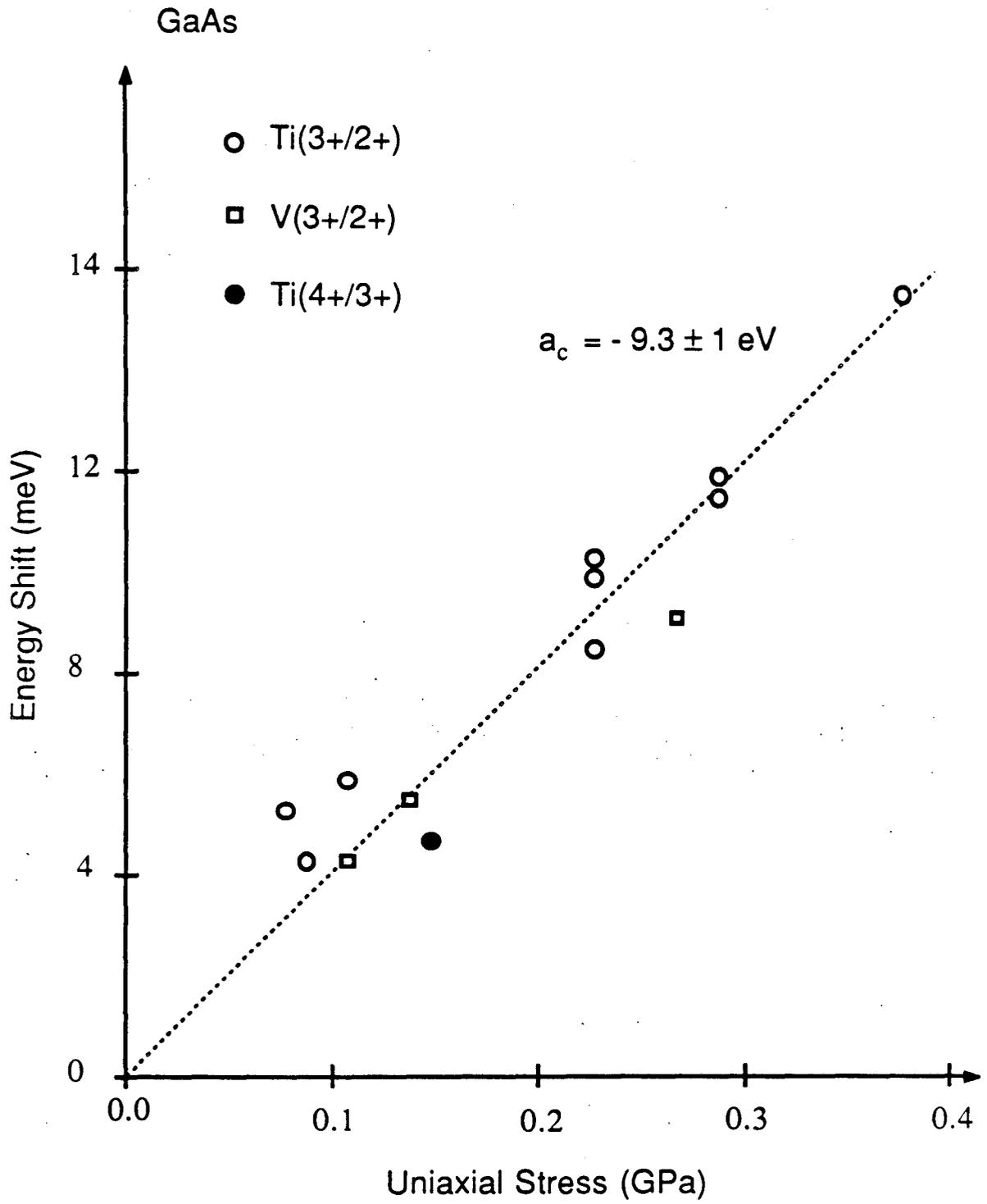
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Figure 1.



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Figure 2.



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Figure 3.

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