Temperature dependence of the band overlap in InAs/GaSb structures

D. M. Symons, M. Lakrimi, M. van der Burgt, T. A. Vaughan, R. J. Nicholas, N. J. Mason, and P. J. Walker

Physics Department, Clarendon Laboratory, The University of Oxford, Parks Road, Oxford, OX1 3PU, United Kingdom

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We have studied the temperature dependence of the band overlap in InAs/GaSb structures by performing magnetotransport measurements on both semiconducting and semimetallic superlattices at temperatures between 110 and 340 K and in fields up to 45 T. Semiconducting samples have very few carriers at 4 K, but at these higher temperatures intrinsic carriers are thermally excited across the energy gap. By measuring the variation of the electron and hole densities with temperature it is possible to determine the energy gap between the electron and hole confinement energies and thus the band overlap between the InAs conduction band and the GaSb valence band. We find that this overlap is 30 meV larger at 300 K than at 4 K, which agrees with similar measurements on a semimetallic sample and also the model-solid theory of Van de Walle.

I. INTRODUCTION

In this paper we have performed an accurate study of how the band offset between two semiconductors varies with temperature. We have investigated the extreme type-II system InAs/GaSb, which is a very good materials combination for studying band offsets because of the crossed gap lineup, which is shown schematically in Fig. 1. The conduction band of InAs lies below the valence band of GaSb and the measurable properties of the system are very sensitive to the particular value of the band offset at the interface. It is also possible to dramatically alter the properties of such a structure by changing the layer thicknesses.[1] For sufficiently thin layers, the confinement energies of the electrons in the InAs layers and the holes in the GaSb layers are large enough that the ground subband energy of the electrons lies above that of the holes as shown in Fig. 1. The system is said to be semiconducting and the structure will contain no carriers at low temperatures, but as the temperature is increased carriers will be thermally excited across the energy gap, which can lead to high densities at room temperature. The structure behaves like a bulk intrinsic semiconductor with a narrow band gap that can be tuned by varying the layer thicknesses. Omaggio *et al.*[2] have used the temperature dependence of the carrier density to determine the zero temperature extrapolated energy gap. If the layers are thicker, the confinement energies are smaller and the ground electron subband energy will fall below that of the holes. The system is now semimetallic and electrons will transfer from the GaSb valence band to the InAs conduction band. This results in large densities of both two-dimensional (2D) electrons and 2D holes even at low temperatures.[3]

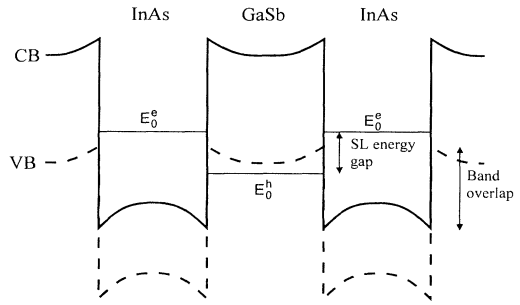

FIG. 1. Schematic diagram of a semiconducting InAs/GaSb SL. The band overlap is the energy difference between the InAs conduction band and the GaSb valence band and the SL energy gap is the difference between the electron and hole confinement energies. If the layer thicknesses are increased, E_0^e falls below E_0^h and the SL becomes semimetallic.

In the InAs/GaSb system all the properties are very sensitive to the particular value of the overlap between the InAs conduction band and the GaSb valence band, which can be altered by many different methods. Hydrostatic pressure decreases the overlap and the application of about 15 kbar will reduce it to zero and cause a semimetallic structure to become semiconducting.[4,5] Alloying indium into the GaSb increases the overlap and the carrier densities of InAs/(Ga,In)Sb structures are always larger than equivalent InAs/GaSb structures.[6] Structures grown with a [111]*A* orientation have an overlap 60 meV larger than for those grown along [001], which is attributed to the presence of a dipole at the [111]*A* interface.[7] The atomic stacking sequence at the interfaces can be arranged to give either a monolayer of InSb or alternatively a monolayer of GaAs. We find that the carrier densities are larger for the interface with a monolayer of InSb and hence so is the band overlap.[8] In this paper we use two carrier measurements of the electron and hole densities, together with the known band parameters, to calculate the energy gap and the band overlap as a function of temperature. We show that increasing the temperature causes the band overlap to increase, thus reducing the energy gap between the electron and hole confinement energies.

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II. EXPERIMENTAL DETAILS

We have studied two InAs/GaSb superlattices (SL); the first is semiconducting with 100 periods of thickness 70 Å InAs and 75 Å GaSb and the second is semimetallic with 20 periods of 160 Å InAs and 105 Å GaSb. The layer thicknesses were measured by transmission electron microscopy (TEM) and x-ray diffraction (XRD).[9] The SL were grown using atmospheric pressure metal-organic vapor phase epitaxy (MOVPE) on a semi-insulating GaAs [001] substrate, which was first precoated with a 1 μm GaSb buffer layer. For the shorter period SL, when changing from the growth of InAs to GaSb, the switching sequence of the sources was configured so that the interface was GaAs-like, but the second interface going from GaSb to InAs was configured to be InSb-like. These interfaces were found to have the best structural quality as deduced from observation of the folded longitudinal acoustic phonons by Raman measurements and also from high resolution TEM measurements.[9] For the longer period SL, both interfaces were configured to be InSb-like. We have performed magnetotransport measurements of the Hall resistivity and the magnetoresistivity at temperatures between 110 K and 340 K in a pulsed field coil giving fields up to 45 T, applied perpendicular to the active layers. The temperature was measured using a calibrated silicon diode placed close to the sample.

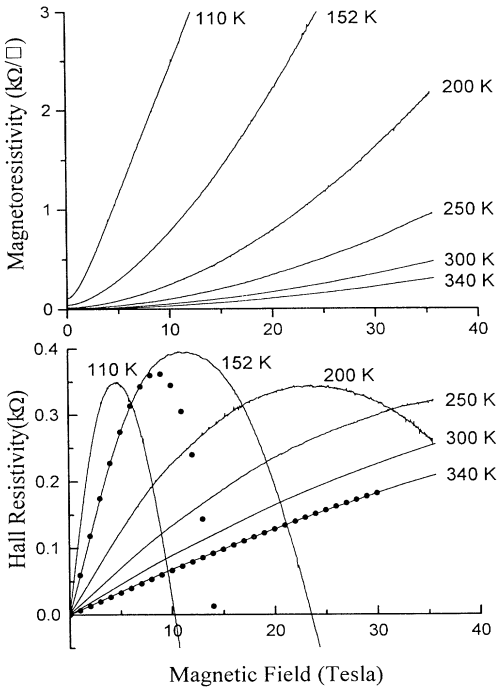

FIG. 2. Measured Hall resistivity and magnetoresistivity traces for the 100-period semiconducting SL. The points show the fitted data for the 340 K and 152 K traces.

III. RESULTS

A. Semiconducting sample

First, we will discuss the results of the semiconducting SL whose magnetotransport traces are shown in Fig. 2. The slope of the Hall resistance at low field is determined mainly by the electron density in the SL since the electrons have a much larger mobility than that of the holes. As the temperature is increased this slope decreases because more electrons are thermally excited across the energy gap. At all temperatures, the Hall resistance traces are curved at higher fields, which is indicative of both electrons and holes contributing to the conduction in the SL. At the lower temperatures the Hall voltage changes sign at high field which shows that the overall hole density is larger than that of the electrons, but that the holes have a much smaller mobility. As the temperature is increased the field at which the Hall voltage changes sign shifts upward and for the higher temperatures is beyond the maximum field to which we can measure. Even at the highest temperature though, the Hall resistance trace bends down, which is consistent with a hole density that is still larger than that of the electrons. The additional extrinsic hole density comes mainly from the parallel conduction taking place in the 1 μm nominally undoped, but in practice slightly p-type, GaSb buffer layer.

It is possible to deduce electron and hole densities at each temperature by fitting the Hall traces to the classical two-carrier expression.[10] The fits produced are quite good, but tend to deviate from the measured traces at high fields and low temperatures. This is because the magnetic quantization causes a strong change in both the density of states and the energy gap of the SL, which increases with field due to the increase in zero point motion energy of the lowest Landau levels of the electrons and the holes, of $\frac{1}{2}\hbar\omega_c^e$ and $\frac{1}{2}\hbar\omega_c^h$, respectively, where ω_c^e and ω_c^h are the cyclotron frequencies of the electrons and holes. The energy of the ground electron Landau level increases by about 50 meV between zero and 40 T, which means that together with the corresponding increase of about 8 meV in the hole Landau level energy the energy gap of the SL at 40 T is about 60 meV larger than at zero field. We have therefore performed fits both neglecting and including the effects of magnetic fields.

We shall now outline the method we have used to fit the carrier densities in detail and how these can be used to calculate the energy gap of the SL. The InAs wells are thin and the electron mass is small, so the separation between the ground and first electron subbands is very large (~250 meV) and thus even at the very highest temperatures all the electrons will be in the ground subband. The density of states of the electrons is therefore truly two dimensional. Conversely, the mass of the holes in the GaSb is very much larger and therefore the hole subbands are not very well separated. At 300 K the ground 2D hole subband lies about 75 meV below the Fermi energy. $\mathbf{k}\cdot\mathbf{p}$ calculations show that at least two other strongly interacting hole subbands lie within 100 meV of the ground subband.[11] The density of states for the holes is therefore likely to be reasonably well described by a three-dimensional picture. The electron and hole densities are calculated using the Fermi-Dirac dis-

tribution functions f_e and f_h and the density of states functions D_e and D_h for the electrons and the holes and are related to the energy gap of the SL and its chemical potential μ. The band edge effective masses used are $0.023\ m_0$ for the electrons and $0.3\ m_0$ for the holes. Nonparabolicity is included for the electrons in the same way as described in Ref. 5 The carrier densities n_e and n_h of the electrons and holes, respectively, are given by

$$n_e = \int_{E_0^e}^{\infty} D_e(E)\, f_e(E)\, dE\ ,$$

$$n_h = \int_{-\infty}^{E_0^h} D_h(E)\, f_h(E)\, dE\ ,$$

where

$$f_e(E) = \frac{1}{1+\exp\left[(E-\mu)/k_BT\right]}$$

and

$$f_h(E) = 1 - f_e(E)\,.$$

The band overlap in this crossed gap system is a very important parameter since it has a very large effect on all the properties of any such structure. We calculate self-consistent values for the electron confinement energy E_0^e and the hole confinement energy E_0^h, which are temperature dependent due to the changes in the carrier densities, taking into account the band bending in the layers due to the confined electrons and holes.[5] We can thus determine how the band overlap varies with temperature using the energy gap of the SL, which is given by the energy of E_0^e relative to E_0^h, as illustrated in Fig. 1.

For each temperature we have calculated how the carrier densities vary with magnetic field. We have used a semielliptic density of states with constant broadening for the electron Landau levels and a 3D density of states for the holes which we shift down in energy as the field is increased due to increase in the zero point motion of the holes. At each field it is necessary to recalculate the position of the chemical potential such that the difference between the electron and hole densities remains constant. Although the energy gap increases very quickly with magnetic field, the carrier densities do not decrease as quickly as might be expected as several Landau levels are partially populated at high temperatures. For a 2D electron density of 8×10^{11} cm^{-2} (the 300 K value), four Landau levels would be populated at 10 T and zero temperature. The Landau level separation at 10 T is about 25 meV and at high temperatures the extra thermal energy will cause more levels to be populated. We find that at 300 K the carrier densities are reduced by about 5% when a field of 30 T is applied, but that the field-induced decrease is close to 50% when the temperature is reduced to 150 K.

For each of the temperatures, we have fitted the Hall voltage using the classical two carrier expressions,[10] but with electron and hole densities which vary with field. This yields an energy gap at zero magnetic field along with the low field mobilities of the electrons and the holes. The electrical parameters are given for each of the measured temperatures in Table I. The extrinsic density is determined by the density of dopants within the SL which will not change rapidly with temperature. The extrinsic density yielded by the fitting remains almost constant with temperature and is always much smaller than the intrinsic density. The electrons and the holes are confined in adjacent layers and have almost equal densities at all temperatures. Hence the temperature dependence of the scattering of the carriers, which determines their mobility, is likely to be similar for the two carrier types. It is therefore encouraging that the ratio of the electron mobility to the hole mobility does not change much with temperature, as can be seen in Table I. The fits are very good at high temperatures, but when the temperature is reduced the fit is only good at low fields, as shown in Fig. 2. This is probably partly due to some parallel conduction in the GaSb buffer layer. The bulk GaSb grown in the same MOVPE reactor typically has a p-type density of $(5\text{–}10)\times10^{15}$cm^{-3}, giving an equivalent 2D density for the 1 μm buffer of $(5\text{–}10)\times10^{11}$ cm^{-2}, which is comparable to the total measured extrinsic density of the SL and is therefore likely to greatly affect the Hall resistance at high field.

The energy gap which we deduce is found to be 19 meV at 340 K and increases as the temperature is reduced, reaching 51 meV at 150 K, as shown in Table I and Fig. 3. The energy gap of this sample has been deduced to be 65 meV by measuring the interband photoconductivity response at 4 K using a Fourier transform

TABLE I. The fitted zero field electron and hole densities per layer n_e and n_h and their respective mobilities μ_e and μ_h for the 100-period semiconducting SL. The energy gap E_g is deduced from these densities and then used to calculate the value for the band overlap Δ. The 4 K value for the SL energy gap was taken from photoconductivity measurements (Ref. 11)

Temperature (K)	n_e (10^{11} cm^{-2})	n_h (10^{11} cm^{-2})	μ_e (m^2/V s)	μ_h (m^2/V s)	E_g (meV)	Δ (meV)
4	0	0			65	120
152	0.8	0.9	1.54	0.18	51	133
200	2.0	2.1	1.26	0.14	45	137
250	3.7	3.9	0.98	0.10	38	141
300	6.0	6.2	1.13	0.09	27	146
340	8.1	8.3	1.12	0.08	19	150

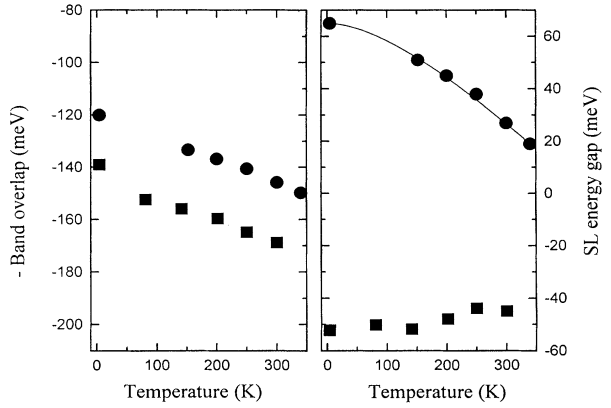

FIG. 3. Band overlap and SL energy gap, plotted with the same scales, of both the semiconducting (circles) and the semimetallic (squares) sample as functions of temperature. The band overlap of the semiconducting sample is about 20 meV smaller at all temperatures because it has interfaces of alternating type, which is explained more fully in the text. The line shows a fit to the semiconducting SL energy gap using the Varshni expression with $A = 0.24$ meV/K and $\theta = 264$ K.

spectrometer,[11] which is consistent with the results from our magnetotransport measurements. The temperature dependence of the SL energy gap comes from two factors. First, there is a change in the relative positions of the conduction band of the InAs and the valence band of the GaSb, and second, there is a change in the self-consistent contribution to the confinement energies, due to the change in carrier densities and therefore of the band bowing in the wells.

The 4 K band overlap in the InAs/GaSb system has been measured to be 140 meV for an InSb interface, but is reduced to 100 meV for a GaAs interface.[7,8] The sample described in this section has alternating interface types and since the confinement energies are a long way above the band edges we would expect the sample to be reasonably well described using a mean value of 120 meV for both interfaces. The layers in this sample are thin and therefore their precise thicknesses have a very large effect on the calculated values of the confinement energies. We know that the period of the SL is (145±5) Å from the TEM and XRD measurements, but these do not give the thicknesses of the individual layers to the same degree of precision. We have therefore fitted the InAs thickness to be (70±5) Å and the GaSb to be (75±5) Å, so that using a 4 K band overlap of 120 meV and an 8×8 $\mathbf{k}\cdot\mathbf{p}$ calculation of the SL energies gives a calculated energy gap of 65 meV to agree with the photoconductivity data.[11] We can then use these layer thicknesses to deduce a precise variation of the band overlap with temperature. The band overlap is found to increase with temperature, as shown in Table I and Fig. 3, but is only increased by about 30 meV by increasing the temperature from 4 K to 300 K, which is about half the change of the band gaps of the constituent bulk materials, given in Table II.

TABLE II. The variation of the bulk band gaps are described by the expression given by Varshni (Ref. 12) and the parameters for A and θ for InAs and GaSb used in this expression are given in the table. ΔE_g gives the change in bulk band gap between 300 K and 80 K, which is close to linear in this range.

	A (meV/K)	θ (K)	ΔE_g (meV)
InAs[a]	0.335	248	50
GaSb[b]	0.48	280	70

[a]Reference 14.
[b]Reference 15.

B. Semimetallic sample

We have also determined how the band overlap of a semimetallic, longer period SL varies with temperature, by the same method as described above for the semiconducting SL. At all temperatures the confinement energy for the electrons lies below that of the holes so that the energy gap is negative and charge transfer occurs between the layers even at zero temperature.

Figure 4 shows the Hall resistance traces of this sample as a function of temperature. At high temperatures, the Hall resistance traces are very similar to those measured for the semiconducting SL in that they bend down, indicating that the hole density is slightly larger than that of the electrons. As the temperature is reduced the carrier densities decrease and when the holes in the GaSb buffer layer freeze out the hole density becomes slightly smaller

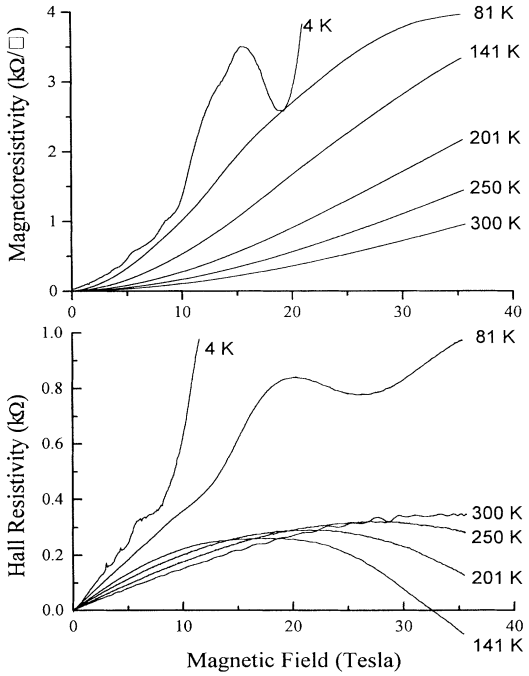

FIG. 4. Measured Hall resistivity and magnetoresistivity traces for the 20-period semimetallic SL.

than that of the electrons. This can be seen for the trace measured at 4 K, which bends up very strongly at high fields.

We have fitted the Hall traces as before, including the magnetic field dependence of the carrier densities. It was necessary to include a second electron subband for this sample due to the wider InAs layer, especially for the higher temperature traces. The energy gap is negative for all the temperatures studied, indicating that the structure is semimetallic, but changes very little with increasing temperature, which is different from the behavior of the shorter period SL, as shown in Fig. 3. The electron confinement energy in these structures is pushed up by the bowing of the bottom of the InAs well due to the confined charge. The magnitude of the band bending is propotional to the electron density and also to the thickness of the well. The longer period SL has more electrons confined in each layer and also thicker layers so that the confinement energies of the electrons and the holes shift more in position relative to the band edges than for the shorter period SL. In the semimetallic SL the temperature dependence of the self-consistent contribution to the energy gap almost exactly cancels the temperature-induced change in the band overlap.

The electron and hole densities per layer were measured to be 5.0×10^{11} cm^{-2} and 4.9×10^{11} cm^{-2} at 4.2 K, which we have used to calculate a band overlap of 140 meV using the method described in Ref. 7 and is in good agreement with our previous measurements. As the temperature rises, we find, as for the other sample, that the band overlap increases by ~30 meV as the temperature is increased from 4 K to 300 K, as shown in Fig. 3. This provides excellent corroboration of the results of the previous sample, since the two structures have very different electrical properties, especially at low temperatures, but yet yield the same rate of change of band overlap with temperature.

IV. DISCUSSION

As the temperature is increased the band gaps of bulk materials decrease, following the relation given by Varshni[12]

$$E_g(T) = E_g(0) - A\frac{T^2}{T+\theta},$$

such that the energy gap hardly changes at low temperatures, but becomes almost linear in the temperature range covered by this experiment. The coefficients A and θ for bulk InAs and GaSb are given in Table II. The temperature-induced change in the band overlap is considerably smaller than the change in the bulk band gaps of the constituent materials, although the energy gap of the semiconducting SL is seen to decrease by a similar amount due to the additional change caused by the self-consistent potential. The temperature dependence of the semiconducting SL energy gap is described quite well by the Varshni expression with $A = 0.24$ meV/K and $\theta = 264$ K, as shown in Fig. 3.

The model-solid theory of Van de Walle[13] gives values

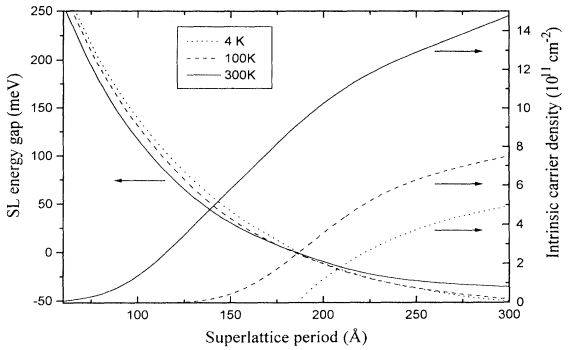

FIG. 5. Calculated intrinsic carrier density and energy gap of a SL with equal InAs and GaSb thicknesses versus SL period for three different temperatures. Semiconducting behavior is observed at low SL period and semimetallic behavior when the period is larger. A band overlap of 140 meV is used at 4 K, 150 meV at 100 K, and 170 meV at 300 K, in line with the findings of this paper.

for the deformation potentials of the individual bands of many semiconductors. These describe how the bands move relative to a fixed potential when the volume of the crystal is changed. The shift in position of the conduction band ΔE_c, produced by a temperature change ΔT is given by

$$\Delta E_c = a_c 3\alpha \Delta T,$$

where a_c is the deformation potential of the conduction band and α is the linear thermal expansion coefficient of the bulk material. Using this relation and a similar one for the valence band, we estimate that the band overlap will increase by 25 meV when the temperature is increased from 4 K to 300 K. This is in very good agreement with the values measured for both the samples described in this paper. This is to be expected, given the excellent agreement found with the pressure measurements using the same theoretical approach.[5]

The parameters deduced from this analysis now allow us to use $\mathbf{k}\cdot\mathbf{p}$ theory calculations of the SL energy gap, in combination with the analysis described above, to calculate the intrinsic carrier density as a function of superlattice period. This is shown in Fig. 5 at 300, 100, and 4 K, for a superlattice with equal InAs and GaSb thicknesses, together with the SL energy gap. This shows how a simple Hall measurement at 300 K can be used to give a good estimate of the energy gap and even the layer thicknesses of the SL.

V. CONCLUSION

We have performed magnetotransport measurements on both a semiconducting and a semimetallic InAs/GaSb SL at temperatures from 4 K up to 340 K, which have allowed us to measure the energy gap of the structures as a function of temperature. We have also calculated how the band overlap varies with temperature for both

samples and we find that it is increased by about 30 meV when the temperature is raised from 4 K to 300 K. This change with temperature is roughly half the change of the band gaps of the constituent bulk semiconductors, but is consistent with estimates based on the model-solid theory. This is a measurement of how the band offset at an interface varies with temperature, which is possible because of the peculiar band lineup in this system. Furthermore, the results of this paper suggest that the model-solid theory may be used to correctly predict the effect of temperature.

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[1] L. L. Chang, J. Phys. Soc. Jpn. **49**, 997 (1980).
[2] J. P. Omaggio, J. R. Meyer, R. J. Wagner, C. A. Hoffman, M. J. Yang, D. H. Chow, and R. H. Miles, Appl. Phys. Lett. **61**, 207 (1992).
[3] M. Lakrimi, R. W. Martin, C. López, D. M. Symons, E. T. R. Chidley, R. J. Nicholas, N. J. Mason, and P. J. Walker, Semicond. Sci. Technol. **8**, S367 (1993).
[4] J. Beerens, G. Grégoris, J. C. Portal, E. E. Mendez, L. L. Chang, and L. Esaki, Phys. Rev. B **36**, 4742 (1987).
[5] D. M. Symons, M. Lakrimi, R. J. Warburton, R. J. Nicholas, N. J. Mason, P. J. Walker, M. I. Eremets, and G. Hill, Phys. Rev. B **49**, 16 614 (1994).
[6] K. S. H. Dalton, M. van der Burgt, M. Lakrimi, R. J. Warburton, M. S. Daly, W. Lubczyński, R. W. Martin, D. M. Symons, D. J. Barnes, N. Miura, R. J. Nicholas, N. J. Mason, and P. J. Walker, Surf. Sci. **305**, 156 (1994).
[7] D. M. Symons, M. Lakrimi, R. J. Warburton, R. J. Nicholas, N. J. Mason, P. J. Walker, and M. I. Eremets, Semicond. Sci. Technol. **9** 118 (1993).
[8] M. S. Daly, W. Lubczyński, R. J. Warburton, D. M. Symons, M. Lakrimi, M. van der Burgt, K. S. H. Dalton, R. J. Nicholas, N. J. Mason, and P. J. Walker, J. Phys. Chem. Solids (to be published).
[9] G. R. Booker, P. C. Klipstein, M. Lakrimi, S. Lyapin, N. J. Mason, R. J. Nicholas, T.-Y. Seong, D. M. Symons, T. A. Vaughan, and P. J. Walker, J. Cryst. Growth (to be published).
[10] M. J. Kane, N. Apsley, D. A. Anderson, L. L. Taylor, and T. Kerr, J. Phys. C **18**, 5629 (1985).
[11] T. A. Vaughan, M. Lakrimi, R. J. Nicholas, N. J. Mason, and P. J. Walker, Proceedings of the 22nd International Conference on the Physics of Semiconductors (World Scientific, Singapore, in press).
[12] Y. P. Varshni, Physica **34** 149 (1967).
[13] C. G. Van de Walle, Phys. Rev. B **39** 1871 (1989).
[14] *Numerical Data and Functional Relationships in Science and Technology,* edited by O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a (Springer-Verlag, Berlin, 1982).
[15] A. Krier, S. A. Bissitt, N. J. Mason, R. J. Nicholas, A. Salesse, and P. J. Walker, Semicond. Sci. Technol. **9**, 87 (1994).