

Reply to "Comment on 'Binding and formation energies of native defect pairs in GaAs'"

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Hurle's analysis of the experimental data suggests that one of the two reactions which we predicted might not occur. His reasoning contains one experimental link which is somewhat weaker than the others in that, although it is likely to be correct, it needs to be checked. If the cited reaction does in fact not occur, the reason may be kinetic, not thermodynamic.

Hurle's comment¹ deals with our calculation² of the Fermi-energy (E_F)-dependent reaction energies $\epsilon_1(E_F)$ and $\epsilon_2(E_F)$ which are associated with the reactions

$$V_{\text{Ga}} \rightarrow V_{\text{As}} - \text{As}_{\text{Ga}} + \epsilon_1(E_F), \quad (1)$$

$$V_{\text{As}} \rightarrow V_{\text{Ga}} - \text{Ga}_{\text{As}} + \epsilon_2(E_F). \quad (2)$$

We had found that both energies change sign as E_F is swept across the gap. Since the sign of this energy governs which of the two sides of the reaction is the stable one, our findings imply that each of the two reactions will go to one side in *n*-type material and to the other side in *p*-type. The essence of Hurle's comment is that the experimental fact that Ga-rich GaAs can be doped *n*-type shows that reaction 2 is *not* driven to the right in *n*-type material at liquid-phase epitaxy (LPE) temperatures, contrary to what our calculation would seem to imply.

The arguments which Hurle uses to reach this conclusion are based on his assumptions about the background native-defect concentrations in GaAs. Hurle's Ref. 4 contains an impressive collection of data which can be nicely accounted for under the assumptions that he has made. We are not aware of any reason to argue with the beautiful analysis that he has made therein. Therefore, except for one caveat to be mentioned below, we would have to agree that, as Hurle concludes, the self-compensation mechanism implied by Eq. (2) does not occur at LPE temperatures.

The caveat is the following: the arguments which Hurle uses, and with which his logic forces us to agree, lead to the conclusion that autocompensation should be seen up to donor doping levels of the order of the concentration of native arsenic vacancies. He then quotes recent

positron-annihilation results (which show arsenic vacancies in *n*-type as-grown material at a concentration of 10^{17} – 10^{18} cm⁻³) to conclude that, had reaction (2) occurred, autocompensation should have been observed up to this concentration of donors. One has to be sure that the material showing no donor self-compensation does, in fact, have an arsenic vacancy concentration as high as that studied in the positron annihilation experiments. This is a matter which is probably easy to verify.

Still at issue, however, is the reason that the reaction does not occur, if in fact it does not. Reasonable numerical uncertainties in our calculated reaction energy can certainly lessen the driving force for that reaction, although we had not thought that they would be big enough to eliminate it altogether. There is an open question regarding the height of the barrier (we expect the reaction to be thermally activated but we have not calculated the activation energy) which translates into the following kinetic consideration: At the highest temperatures, the doped crystal is intrinsic and becomes (say) *n*-type only as the temperature is lowered. At LPE temperatures, is the Fermi energy high enough to drive reaction (2) to the right, and is the barrier low enough to allow the reaction to proceed? LPE is certainly the lowest-temperature growth process and one would be curious to know if the reaction does occur under higher-temperature treatments which are known to change the compensation.³⁻⁵

Hurle suggests that our neglect of the entropy might provide an alternative explanation. This is possible, but the intrinsic numerical uncertainty of our calculations is much larger than the reasonable estimate of the temperature-entropy product, even at growth temperatures.

¹D. T. J. Hurle, preceding paper, Phys. Rev. B **39**, 8005 (1989).

²G. A. Baraff and M. Schlüter, Phys. Rev. B **33**, 7346 (1986).

³J. M. Woodall and J. F. Woods, Solid State Commun. **4**, 33 (1966).

⁴D. C. Look, P. W. Yu, W. M. Theis, W. Ford, G. Matthur, J. R. Sizelove, and S. S. Li, Appl. Phys. Lett. **48**, 1083 (1986).

⁵J. Lagowski, H. C. Gatos, C. H. Kang, M. Skowronski, K. Y. Ko, and D. G. Lin, Appl. Phys. Lett. **49**, 892 (1986).