

### Gallium Vacancy and *EL 2* in GaAs

In a recent Letter Baraff and Schlüter<sup>1</sup> report interesting results on the gallium vacancy ( $V_{\text{Ga}}$ ) in gallium arsenide and its potential relationship to the important *EL 2* deep-level defect. In this Comment we report *ab initio* total-energy calculations which reinforce qualitative features of the tight-binding-interpolated *ab initio* calculations described in Ref. 1. We also present additional theoretical predictions for the experimental signature of  $V_{\text{Ga}}$ .

We have performed extensive calculations of the energy surface of  $V_{\text{Ga}}$  using pseudopotential density-functional theory in the supercell approximation.<sup>2</sup> The supercell used contained 64 atoms. In Fig. 1 we show the results of our total-energy calculations as a function of displacement of one of the adjacent As atoms towards the vacancy site. Relaxation includes the breathing mode of the three neighboring As atoms, and, separately, of the three Ga neighbors of the moving As atom (some uncertainty remains near  $R = 0$  because we did not include other Jahn-Teller distortions).

Despite some differences of our results from those of Ref. 1 (e.g., *no* secondary metastable minimum at  $R = 0.3$  and different positions of defect levels crossing into the valence and conduction bands), several conclusions are possible. We find that positively charged  $V_{\text{Ga}}$  is metastable and the stable configuration consists of an intimate  $\text{As}_{\text{Ga}}V_{\text{As}}$  pair. We find a barrier to motion to the ground state of 0.23 eV. It is tempting to identify this metastability with the persistent photoquenching observed for the *EL 2* deep level as discussed in Ref. 1. Such a model would suggest that  $V_{\text{Ga}}$  is the *EL 2* defect disguised as  $\text{As}_{\text{Ga}}V_{\text{As}}$ , and the metastable state is the usual  $V_{\text{Ga}}$  geometry. However, this correspondence proves to be illusory as we now show by describing the signature of the defect  $V_{\text{Ga}}$  including the possible transformation to  $\text{As}_{\text{Ga}}V_{\text{As}}$ .

The overall thermodynamic energy level diagram for this defect is highly unusual. The two configurations with very different electronic structures lead to stability of  $(+++)$  ( $\text{As}_{\text{Ga}}V_{\text{As}}$ ) for Fermi energies up to  $\sim 0.5$  eV above the valence band. Beyond  $\sim 0.7$  eV the  $(---)$  ( $V_{\text{Ga}}$ ) is stable. Our results, combined with the electronic structure of Ref. 1 for highly charged states, yields the transitions  $(+++/- - -)$ ,  $(- - -/+ - -)$  at 0.5, 0.7 eV (remarkable negative effective correlation energy).

This thermodynamic level structure will only be relevant for experiments when the necessary structural transformations are possible. For room-temperature *n-type* material the equilibrating transition  $(+++)$  ( $\text{As}_{\text{Ga}}V_{\text{As}}$ )  $\rightarrow$   $(---)$  ( $V_{\text{Ga}}$ ) by successive electron capture involves a structural barrier of  $0.05 \pm 0.2$  eV along the (0) energy surface or at most  $0.6 \pm 0.2$  eV along the (+) energy surface. This implies a transi-

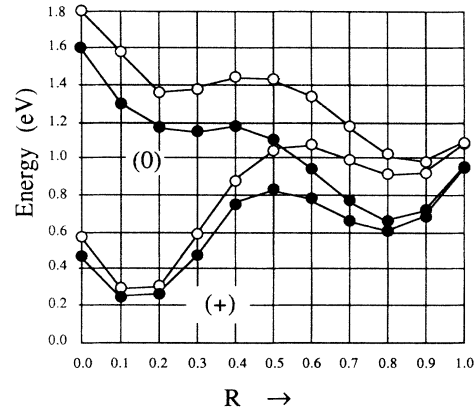


FIG. 1. Total energy of  $V_{\text{Ga}}$  for (+) and (0) charge states as a function of displacement of an adjacent As into the vacancy site (horizontal axis convention as in Fig. 1 of Ref. 1 with  $R = 1$  the ideal vacancy). Open circles are rigid lattice values, solid circles include relaxation. The relative energy of (+) and (0) is set as for *p-type* material.

tion time of at most  $10^{-2 \pm 3}$  sec for equilibration. Thus, in room-temperature material this defect should be completely equilibrated.

With this result, experiments apparently rule out this defect's yielding the dominant deep level, since common experimental procedures rule out a strongly accepting dominant midgap state.<sup>3</sup> In a depletion region of reverse-biased diodes used for photoquenching experiments the state of this defect will be determined by the sequence of temperature and illumination treatments.

To identify  $V_{\text{Ga}}$  we suggest the following experimental signatures. First, to enhance the concentration of  $V_{\text{Ga}}$  over  $\text{As}_{\text{Ga}}$ , or its complexes, quenching might be used. The strongly amphoteric nature of this defect having donor and acceptor *optical* transitions overlapping within the gap is then likely to be a distinctive feature. We are also currently studying other configurations of  $V_{\text{Ga}}$  to see if they affect its properties.

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Y. Bar-Yam and J. D. Joannopoulos

Department of Physics  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

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<sup>1</sup>G. A. Baraff and M. Schlüter, Phys. Rev. Lett. 55, 2340 (1985).

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<sup>3</sup>A. Mircea, A. Mitonneau, L. Hollan, and A. Brière, Appl. Phys. 11, 153 (1976); E. Weber and J. Lagowsky, private communication.