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Systematic approach to distinguishing a perturbed host state from an impurity state in a supercell calculation for a doped semiconductor: Using GaP:N as an example

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We illustrate a systematic approach for distinguishing a perturbed host state from an impurity state in a supercell calculation for a doped semiconductor, using GaP:N as an example and employing a charge-patching technique based on a first-principles pseudopotential method. For GaP:N, we (1) identify an impuritylike state that is resonant with the conduction band minimum in the dilute doping limit, which provides a qualitative explanation for the peculiar behavior of the A_x transition; (2) provide an alternative explanation of a recent finding of the existence of multiple impurity states resonant within the conduction band up to the energy of the Γ point; and (3) show that there exists no impurity state caused by a valley-orbit interaction within a few hundred meV proximity of the N bound state, in contrast to the decades long speculation of the existence of such a state.

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The impurity potential introduced by an isoelectronic impurity in a semiconductor is generally considered highly localized, and thus can only give rise to a very limited number of impurity states.[1,2] In perhaps the best-studied isoelectronic impurity system, GaP:N, an isolated N center was consistently found to have only one impurity state (IS), a bound state with a_1 symmetry of T_d, near the conduction band (CB) minimum (CBM) in theoretical calculations using either the empirical pseudopotential or Koster-Slater model, when a highly localized impurity potential was assumed.[2–4] Only when a "long-range" component was artificially introduced into the impurity potential to simulate the effects of lattice relaxation and electronic polarization, was it possible to generate an excited state with e symmetry lying close to the a_1 state, resembling the valley-orbit coupling for a Columbic impurity, because the valley-orbit coupling is expected to be very large for the short-range potential.[2] Experimentally, the existence of such an e symmetry excited state for the bound electron was speculated for the isolated N center to be 24 meV above a_1 (i.e., above the CBM),[5] as well as for NN_1 (the nitrogen pair center with the deepest bound state) $\sim$80 meV below the CBM.[6] Although the early studies were only concerned with the existence of one excited state caused by the valley-orbit coupling effect,[2,5,6] a recent empirical pseudopotential (EP) calculation using a supercell approach has concluded that the isolated N, as well as N pairs, may introduce multiple additional IS's (the so-called "N cluster states") between the CBM and the CB Γ point (CBΓ).[7] Such a finding is rather surprising, because for an impurity with a highly localized potential, if it has already produced a bound IS, as in the case of GaP:N, usually there will not be another resonance IS, according to a scattering theory for solids.[1] Besides its significance for the above mentioned issues, understanding the electronic structure of GaP:N in the dilute limit should lay the groundwork for understanding the highly interesting nonconventional GaPN alloys, which is currently a field of major controversy.[7–9]

A supercell approach is frequently adopted for investigating impurity or defect states in semiconductors. One typically needs to use a sufficiently large supercell to ensure the convergence of the impurity level[10] and track the origin of the state of interest to the dilute doping limit.[11] However, the use of a supercell inevitably causes a folding effect in k space, i.e., one typically gets a large number of states in each k point of the supercell Brillouin zone. Such a folding effect makes it nontrivial to identify an IS that happens to be resonant with the host conduction or valence band and to differentiate a genuine IS from a folded but perturbed host state (PHS). Thus, it is an issue of general interest how to distinguish an IS from a PHS in the supercell approach.

Because of the above-mentioned controversy and speculations involving GaP:N, we will use this system to illustrate a systematic approach for categorizing the electronic states obtained in a large supercell calculation. For an isolated N in GaP:N, we show that no excited state can be formed within the energy window of CBM-CBΓ. However, we identify one additional a_1 impuritylike state that extrapolates to the CBM in the dilute N limit. This state could be responsible for the so-called A_x transition induced by N doping, which has been observed for decades[12] but not well understood.[9]

The electronic band structure of GaP:N is calculated using a charge-patching method (i.e., reassembling of charge motifs).[13] This method is based on a self-consistent first-principles pseudopotential approach in the framework of density functional theory within a local density approximation (LDA). The band structure calculated with the reassembled charge density is typically accurate to within a few meV of the direct self-consistent calculation with or without the impurity. This method has been shown to describe accurately for GaAs:N the shift of the GaAs host bandgap in the dilute N doping region that is typically not accessible to the direct self-consistent calculation.[14] The Ga pseudopotential is generated with a nonlocal core correction and the 3d states are not included in the valence electrons. The energy cutoff for the plane wave basis is 35 Ry. The valence force field method is used to relax the atomic positions. Empirical corrections to the nonlocal pseudopotentials of Ga, P, and N atoms are introduced to fix the LDA errors in the band gap as well as the intervalley separations (e.g., Γ-L and Γ-X).[15] Other computational details can be found in previous

publications.[13,15] The supercell is a cubic box with a multiplication factor n along three directions of the basic zinc blende cubic cell, with one N atom at the center of the supercell and n up to 12 (or 13 824 atoms).

GaP and N impurity levels in GaP:N. The direct LDA calculation for GaP yields band gaps at X, L, and Γ point as $E_{gX}=1.524$ eV, $E_{gL}=1.621$ eV, and $E_{g\Gamma}=1.757$ eV. The CBM is found at $\mathbf{k}_{\min}=(q_{\min},0,0)k_0$ with $q_{\min}=0.87$ and $k_0=2\pi/a_{\mathrm{GaP}}$ ($a_{\mathrm{GaP}}=5.447$ Å), showing a camel's back structure,[16] with $E_g(\mathbf{k}_{\min})=1.491$ eV. The energy order qualitatively agrees with experimental results, but quantitatively exhibits large disparities that are due primarily to the limitations of the LDA (e.g., calculated $E_{g\Gamma}$-$E_{gX}=0.233$ eV vs experimental value 0.537 eV). The a_1 bound state of an isolated N impurity is found to be at 8 ± 0.5 meV below $E_g(\mathbf{k}_{\min})$, by extrapolating to zero N concentration, which agrees rather well with the experimental result of <11 meV,[12] and early theoretical estimates of 3–6 meV,[4] and is more accurate than the EP result of 60 meV.[17,18] The empirical corrections for the LDA errors yield $E_{gX}=2.350$ eV, $E_{gL}=2.716$ eV, $E_{g\Gamma}=2.887$ eV, and $E_g(\mathbf{k}_{\min})=2.339$ eV with $q_{\min}=0.90$, which reproduces very well the experimental results that include the excitonic effect: $E_{gex}(\mathbf{k}_{\min})=2.328$ eV with $q_{\min}=0.92$ and $E_{gex}(\Gamma)=2.872$ eV.[19] The energy of the isolated N state is then 13.7 meV below $E_g(\mathbf{k}_{\min})$ after the LDA corrections. Because the focus of this work is the impurity excited states generated by the isoelectronic impurity, the implication of this new calculation on the electronic structure of GaPN alloy in general will be discussed elsewhere. After succeeding in accurately reproducing the well-established basic experimental results for both the host band structure and impurity state, we will next proceed to search for the possible impurity excited states in the energy window of interest, if they should exist.

State count and $\mathbf{k}$ *space unfolding*. The first consideration is to count the number of states to see if any additional states are generated, compared to that of the expected folded states in the same supercell without the impurity. If there are M expected folded $\mathbf{k}$ points in a supercell for a given bulk band or energy window, and $M+m$ states have been found in the same supercell but containing one impurity, there must be at least m IS's. A moderate supercell size should be used to ensure that the energy levels of the PHS's and the IS's have not shifted too much from those in the dilute limit, and the number of folded states is not too large to be analyzed. For the energy window of interest, CBM-CBΓ, 512-, and 1728-atom supercells are the appropriate choices. For the 512-atom supercell of GaP (GaP512), 17 states ($4a_1+2e+3t_2$) are found at the supercell Γ point in CBM-CBΓ, with one being the original Γ state and the other 16 being folded states from other $\mathbf{k}\neq0$ points whose energies happen to fall into this energy window. For the 512-atom supercell of GaP:N (GaPN512), we find 18 states instead (i.e., $5a_1+2e+3t_2$). Except for the one a_1 state below the CBM that corresponds to the bound state of an isolated N, all the others can be shown, by projecting their wave functions in k space, to be primarily derived from the same set of states in GaP512, although they have been perturbed to different degrees. Figure 1(a) illustrates the correlation between the states in the supercell and primitive cell for GaPN512, by "unfolding" the supercell $k=0$ states to the GaP dispersion curves according to their largest $\mathbf{k}$ components. In contrast to the finding of multiple IS's in a calculation of GaPN1728,[7] we find no excited IS for GaPN512 within the same energy window. Note that a genuine IS is expected to persist in all supercell sizes, as the a_1 bound state does. In our calculation for GaPN1728

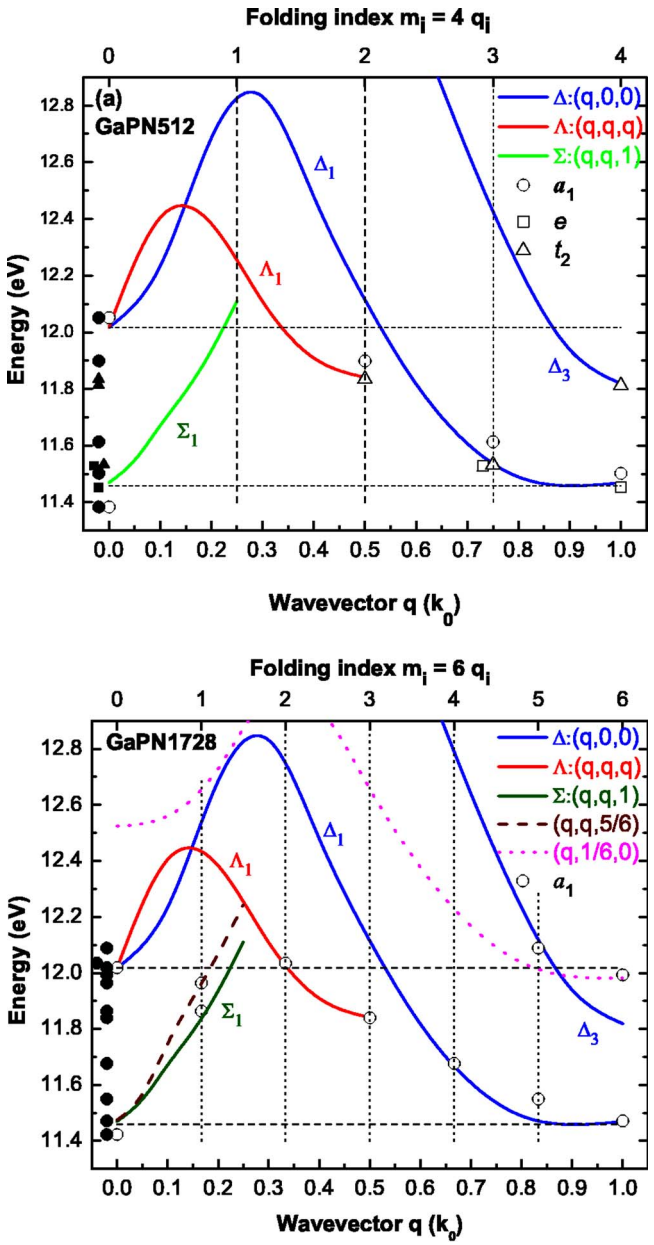

FIG. 1. (Color online) GaP:N conduction band states at the Γ point of supercell Brillouin zone (solid symbols at $q=0$ with circles for a_1, squares for e, and triangles for t_2). They are unfolded to the dispersion curves of GaP (open symbols—supercell Γ states, lines—GaP dispersion curves). The folding index $m_i=nq_i$ with $n=4$ or 6 for the supercell size and $m_i=1,2,\ldots,n$. Two horizontal dashed lines, respectively, indicate the energies of the CBM and CBΓ of GaP. Some data points are slightly displaced horizontally for clarity. (a) For the 512-atom supercell ($n=4$), and (b) for the 1728-atom supercell ($n=6$).

in the same energy window, there are instead 104 states at the supercell Γ point, but still with only one extra a_1 bound state, compared to 103 states for GaP1728. In this counting, 8 equivalent **k** points, $(\pm 1/3, \pm 1/3, \pm 1/3)k0$, with their energies just above that of the Γ point in GaP are also included, because of the proximity of their energies and thus the expected coupling to the GaP Γ point. The $k=0$ states of GaPN1728 can also be unfolded to the GaP dispersions, as shown in Fig. 1(b) (for clarity only the a_1 states are shown).

In general, the unfolding plots like those shown in Fig. 1 not only provide a clear picture as to the origins of the states found in the supercell calculation, but also predict which bulk states are expected to be folded in an energy window of interest. Typically, only the a_1 states exhibit significant energy shifts from the corresponding host states in GaP, which is because the e and t_2 states have zero amplitudes at the impurity site due to the symmetry consideration. For both GaPN512 and GaPN1728, all the e and t_2 states can be clearly associated with their counterparts in GaP512 and GaP1728, and thus there exists no e or t_2 impurity excited state. Therefore, if based solely on the state count, we should conclude that there is no resonant IS in the energy window of interest.

However, the state count does not necessarily yield the correct number of the total IS's. There is a subtle situation in which the IS's are formed at the expense of the same number of host states,[11] and thus there may not always be one-to-one mapping between the perturbed and unperturbed host states based on the folding analysis. This situation is known to occur for the occupied valence band (VB) states. Examples of such IS's may be a hyperdeep a_1 state in GaP:N,[20] a bound state near the VB maximum in GaP:Bi,[21] and a VB resonant impurity level in GaAs:Bi.[11] Although these states could be viewed as extreme cases of PHS's, they are more appropriate to be considered as IS's, because their wave functions away from the impurity site do not resemble those of an extended host state when the impurity concentration approaches zero.[11] To examine such a possibility for the unoccupied CB states in GaP:N, we should further investigate the asymptotic behavior of any suspicious folded states that exhibit the typical signature of an IS: the real-space localization or **k**-space delocalization of its wave function.

Asymptotic behavior of energy level and wave function. The wave function of a PHS is often found to also have a peak at the impurity site in real space, as has been demonstrated in GaAs:N for those folded states derived from the perturbed high symmetry points: $a_1(\Gamma_{1c})$, $a_1(L_{1c})$, and $a_1(X_{1c})$.[15] To decide whether such a state should be considered as an IS or a PHS, it is necessary to examine its asymptotic behavior with varying impurity concentration in two aspects: the energy level at $n \to \infty$ and the wave function at $\mathbf{r} \to \infty$. Figure 2 shows the energy levels of three a_1 states associated with varying supercell size: $E_N(a_1)$, $E_{X1}(a_1)$, and $E_{N^*}(a_1)$, respectively, representing three differently behaving groups. Figure 3 compares the wave functions for these three states in GaPN4096. $E_N(a_1)$ is a trivial IS, because it extrapolates to an energy below the CBM, its wave function diminishes away from the impurity site for large supercells, and there is no missing CB state, at least within the energy

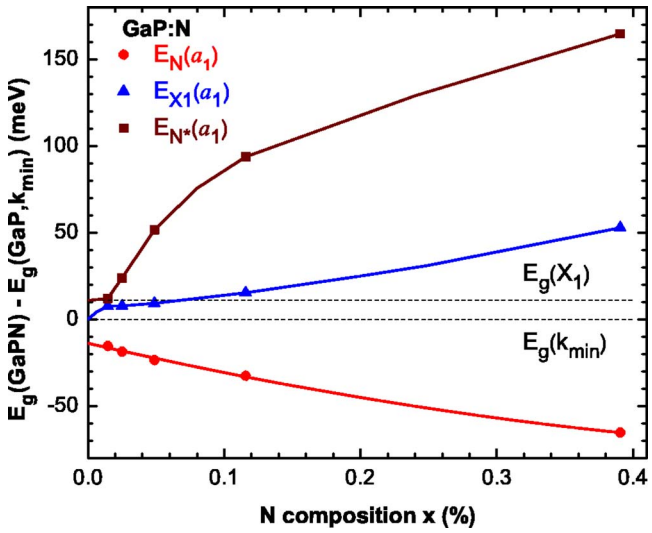

FIG. 2. (Color online) Dependence of the energy level on the nitrogen composition x for three representative states in GaP:N. Solid symbols are calculated values, and the solid lines are drawn as guides to the eyes.

window CBM-CBΓ. $E_{X1}(a_1)$ is identified as a X_{1c}-derived PHS, because it consistently has X_{1c} as the largest component in its wave function, and its energy appears to approach that of X_{1c} for large supercells. Although its wave function shows an enhancement at the impurity site, it becomes bulk-like at sites away from the impurity, which is the typical behavior of a PHS.[11] Usually, there are multiple $E_{X1}(a_1)$-type states deriving from different folded **k** points. $E_{N^*}(a_1)$ is found to involve diverse **k** points in its wave function, but

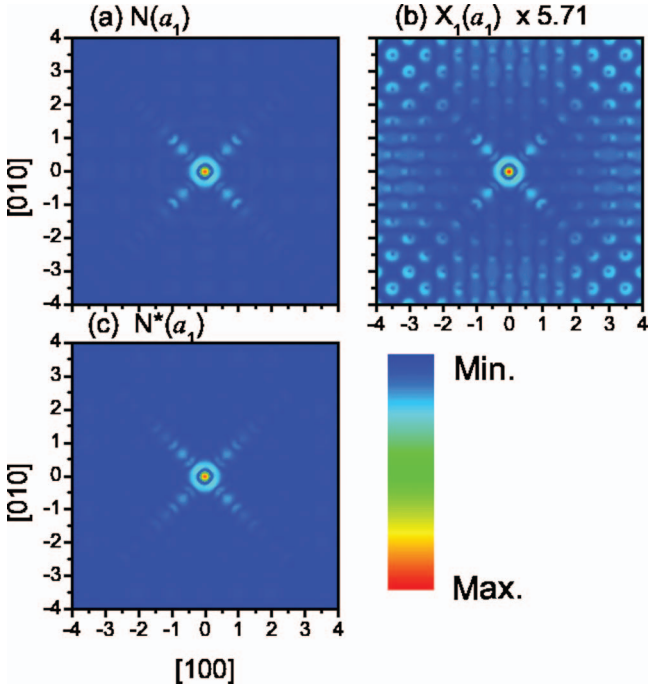

FIG. 3. (Color) Density plots of wave function $|\psi|$ for three a_1 states in the x-y plane containing the N atom in GaPN4096 ($n=8$). The dimensions are in the unit of GaP lattice constant.

without one particular **k** point consistently being the dominant contributor for all supercell sizes. Although very sensitive to the supercell size, this state appears to extrapolate to the CBM at $(q_{\min},0,0)$ (within 1 meV). Its wave function remarkably resembles that of $E_N(a_1)$, only with slightly more extension from the impurity site. For GaPN1728, we find only one $E_{N^*}(a_1)$-type state in the energy range CBM-CBΓ. Practically, such a state may be viewed as an IS, although it seems to become more hostlike in larger supercells (e.g., $n=12$). Thus, this could be considered as a hostlike state that has been most strongly perturbed by the impurity, because of its proximity to the IS. We may now conclude that in the energy window CBM-CBΓ there is no nitrogen IS, and those "N-cluster states" reported previously could actually be misidentified PHS's.[7]

We believe that $E_{N^*}(a_1)$ is responsible for the A_x absorption peak in GaP:N that appears almost exactly at the energy of the GaP indirect excitonic band edge E_{gx}.[12] Interestingly, the A_x peak is found to quickly become unresolvable when the N composition approaches 0.1%.[9] This peculiarity seems to be at least partially related to the interaction of $E_{N^*}(a_1)$ and $E_{X1}(a_1)$ in the dilute doping region. Upon closely examining the results for the largest supercells ($n=10$ and 12), we find an anticrossing behavior between $E_{X1}(a_1)$ and $E_{N^*}(a_1)$, as illustrated in Fig. 2. Because $E_{X1}(a_1)$ typically has a much smaller Γ component than $E_{N^*}(a_1)$ (e.g., for GaPN4096, it is 0.012% vs 0.39%), on reaching the anticross point at $x<0.1\%$, the A_x intensity is expected to decrease quickly, which qualitatively agrees with the experimental finding. Apparently, to reveal the anticrossing behavior of $E_{X1}(a_1)$ and $E_{N^*}(a_1)$, it is critical to have the camel's back structure near X_{1c}, which was lacking in previous calculations.[7,17] Nevertheless, a quantitative account for the experimentally observed small energy shift for A_x is still beyond the accuracy of this calculation and also requires the inclusion of other effects (e.g., exciton and random doping) that is beyond the scope of this work.

Without offering any detailed analysis, we would like to simply mention that no second electron bound state is found for the two N pair centers (i.e., [220] and [110]) that are known to have the largest electron binding energies.[4] This should clarify the speculation about the possible existence of such a second bound state.[6] However, these pair centers do introduce a second IS within the CB, an antibonding state of the bound state, as expected.

In summary, we demonstrate how a systematic analysis can be applied to distinguish an impurity state from a perturbed host state in the commonly adopted supercell approach for impurity or defect study. A perturbed host state is a state whose energy and wave function away from the impurity site asymptotically approach to those of a bulk state when the supercell size approaches to infinity. An impurity state is a state whose wave function remains localized at the impurity site when the supercell size continues to increase. For GaP:N, we show that an isolated N center does not introduce any excited impurity states in the conduction band with an energy up to that of the Γ point, which indicates that the behavior of N in GaP is in general agreement with the expectation for a highly localized impurity. An explanation is given for the peculiar experimental observation of the A_x transition.

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[1] J. Callaway, J. Math. Phys. **5**, 783 (1964).
[2] R. A. Faulkner, Phys. Rev. **175**, 991 (1968).
[3] M. Jaros and S. Brand, J. Phys. C **12**, 525 (1978); B. Gil, J. P. Albert, J. Camassel, H. Mathieu, and C. Benoit a la Guillaume, Phys. Rev. B **33**, 2701 (1986).
[4] Y. Zhang and W. K. Ge, J. Lumin. **85**, 247 (2000).
[5] H. Mathieu, L. Bayo, J. Camassel, and P. Merle, Phys. Rev. B **22**, 4834 (1980).
[6] E. Cohen and M. D. Sturge, Phys. Rev. B **15**, 1039 (1977).
[7] S. V. Dudiy, P. R. C. Kent, and A. Zunger, Phys. Rev. B **70**, 161304 (2004).
[8] Y. Zhang, B. Fluegel, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. B **62**, 4493 (2000); I. A. Buyanova, M. Izadifard, W. M. Chen, H. P. Xin, and C. W. Tu, *ibid.* **69**, 201303(R) (2004); B. Fluegel, Y. Zhang, J. F. Geisz, and A. Mascarenhas, *ibid.* **72**, 197301 (2005).
[9] B. Fluegel, Y. Zhang, J. F. Geisz, and A. Mascarenhas, Phys. Rev. B **72**, 073203 (2005).
[10] J. B. Li and L. W. Wang, Phys. Rev. B **67**, 033102 (2003).
[11] Y. Zhang, A. Mascarenhas, and L. W. Wang, Phys. Rev. B **71**, 155201 (2005).
[12] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).
[13] L. W. Wang, Phys. Rev. Lett. **88**, 256402 (2002).
[14] Y. Zhang, B. Fluegel, M. C. Hanna, A. Mascarenhas, L. W. Wang, Y. J. Wang, and X. Wei, Phys. Rev. B **68**, 075210 (2003); Y. Zhang, B. Fluegel, M. C. Hanna, J. F. Geisz, L.-W. Wang, and A. Mascarenhas, Phys. Status Solidi B **240**, 396 (2003).
[15] L. W. Wang, Appl. Phys. Lett. **78**, 1565 (2001).
[16] O. Madelung, *Semiconductors-Basic Data* (Springer, Berlin, 1996).
[17] P. R. C. Kent and A. Zunger, Appl. Phys. Lett. **79**, 2339 (2001).
[18] We have found that small variations in the empirical pseudopotentials for GaN could result in large fluctuations, in the order of 100 meV, of the N impurity levels in GaAs or GaP. An additional parameter was found necessary to fit the experimental data of GaAsN, see L. Bellaiche, Appl. Phys. Lett. **75**, 2578 (1999).
[19] A. A. Kopylov and A. N. Pikhtin, Sov. Phys. Solid State **11**, 510 (1977); P. J. Dean, G. Kaminsky, and R. B. Zetterstrom, J. Appl. Phys. **38**, 3551 (1967).
[20] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980).
[21] F. A. Trumbore, M. Gershenzon, and D. G. Thomas, Appl. Phys. Lett. **9**, 4 (1969).