Long-Lived Resonance States in n-doped AlGaAs

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The electronic properties of localized resonance states in III-V compound semiconductors are analyzed. In general, resonance states recombine rapidly with the band states. However, a new class of resonance states is found to be long-lived if their coupling to the lattice is sufficiently large. The recombination of these states with band states is thermally activated which leads to extremely long lifetimes at low temperatures. Such states can explain recent experiments suggesting long-lived resonance states associated with persistent photoconductivity and "DX centers" in n-doped $Al_{1-x}Ga_xAs$ for $x < 0.2$.

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Recent experiments on InSb[1] and GaAs[2,3] have been interpreted in terms of long-lived resonance states in the conduction band. In GaAs, for example, these states are associated with Ga-site donors. At low temperatures, electrons captured by these states remain localized for up to a day. Such lifetimes are surprisingly long and are more consistent with bound states than resonance states.

Several types of experiments have been interpreted in terms of long-lived resonance states. In one, hydrostatic pressure was used to convert a resonance state of unknown origin into a bound state which could capture an electron.[1] After release of the pressure, the captured electron remained in the resonance state for a long time τ ($\tau \approx 270$ d at $T = 77$ K). In another experiment, highly doped GaAs under hydrostatic pressure was studied at low temperatures.[3] The Hall data suggested that a donor resonance state captured the electrons and that this state pinned the Fermi level when the doping concentration exceeds 2×10^{19} cm^{-3}. Similar results were found for both Si and Sn doping.[3] These and other experiments[2] are consistent with the concept of a long-lived resonance state.

Such a long-lived resonance state must have novel properties. To have an extremely long lifetime, a resonance state's coupling to the band states must be orders of magnitude less than that of the usual resonance states. A "normal" resonance state is a broad (width $\Gamma \approx 10$ meV) superposition of band states and it is therefore short lived (lifetime $\tau = \hbar/\Gamma \approx 10^{-13}$ sec). The lifetime is increased if the band density of states (DOS) is small and if the resonance-state symmetry differs from that of the band states. For example, the longest-lived previously observed resonance states in compound semiconductors, with lifetimes of order nanoseconds, are atomiclike with a symmetry different from that of the band states (Cr d states, for example, in an s-like GaAs conduction band).

In this Letter we show how lattice distortion can produce a long-lived resonance state. Our model yields resonance-state lifetimes which are temperature dependent and can be very long. We show that this model can explain experiments on such states associated with DX centers in GaAs. To be specific, we suggest that substitutional donors, such as Ga-site Si, undergo small lattice relaxation to produce such resonance states in GaAs.[4]

We consider a generic defect (a substitutional impurity, for example) in a direct-gap III-V semiconductor such as GaAs or InSb. We further assume that the electron-attractive central-cell potential of the defect produces a resonance state lying within the conduction-band Γ-point DOS. This state will be principally derived from the L- and X-point DOS.[4,5] Because of the large effective mass of the parent states, the resonance state will be highly localized.[5] Therefore such a state will be strongly coupled to the lattice.[6,7] The resultant lattice distortion, if it is sufficiently large, will lower the electronic energy of this state into the band gap, and the resonance state will become a real bound state. In other words, at energies for which the host DOS is zero, the lifetime of the state will be infinite. However, the total energy, which includes the lattice distortion energy, lies within the conduction-band states. Thus this state experimentally appears to be a resonance state although it is a stable bound state.

This concept can be generalized. Consider a doping concentration such that the Fermi energy E_F lies above the band edge (assume $kT \ll E_F$). If the distorted electronic state were below E_F, its lifetime would be effectively infinite because it could not recombine with electron-occupied band states. Similarly, if the distorted electronic state were lowered into the valence band (in a narrow-gap semiconductor such as InSb, for example), its lifetime would also be infinite. In general, the demarcation energy is the lowest-energy unoccupied state. This energy is the Fermi energy for the case (heavy doping at low temperatures) considered in this paper.

The lattice distortion is the dynamic deviation from the static distortion caused by creation of the defect. In general, it is a superposition of phonons; for our discussion, it may be envisioned as a breathing-mode relaxation around the impurity (an interaction mode).[7] This lattice distortion Q modifies the electronic energy $E(Q)$

of the resonance state. The total energy

$$\Sigma(Q)=E(Q)+\tfrac{1}{2}\kappa Q^2 \tag{1}$$

of the resonance state also includes a lattice distortion energy $\frac{1}{2}\kappa Q^2$ in which κ is a spring constant. In general, this spring constant is different from κ_0, the spring constant when the level is empty. Our focus will be on the class of defects whose undistorted resonance states of energy $E(0)+i\Gamma$ are converted to bound states ($\Gamma=0$) with energy $E(Q_0)$ by a dynamical lattice distortion Q_0.

This argument can be developed in terms of the illustrative configuration-coordinate diagram. The electronic energy of the resonance is described by the well-known linear coupling approximation,

$$E(Q)\approx E_0-fQ, \tag{2}$$

in which $f=-\partial E(0)/\partial Q$ is a force and $E_0\equiv\mathrm{Re}(E(0))$ is the undistorted electronic energy. The total energies of the lowest-energy unoccupied band state and the resonance state are both shown as functions of Q in Fig. 1. The total energy of the band state with electronic energy $\epsilon(k)$ is simply a parabola, $\Sigma_0(\epsilon,Q)=\frac{1}{2}\kappa_0 Q^2$. For this and the other delocalized band states, the coupling to the lattice distortion is negligible and can be ignored. For the resonance state lying at E_0, any given distortion Q linearly lowers the electronic energy and quadratically increases the lattice energy. The total energy $\Sigma(Q)$ of the localized state is the sum of these energies and it is shown as a shifted parabola. The competition between the two contributions leads to an equilibrium distortion $Q_0=f/\kappa$ which minimizes the total energy. The lattice relaxation energy $E_L=\frac{1}{2}\kappa Q_0^2$ defines both the electronic energy

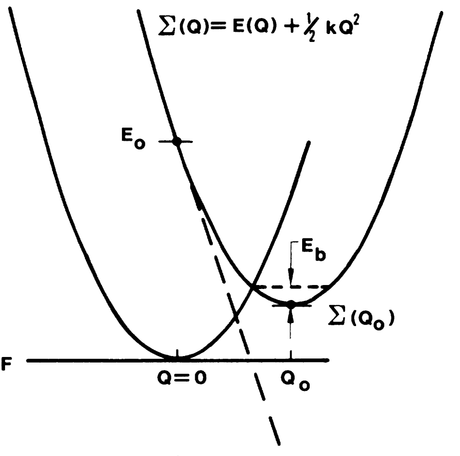

FIG. 1. A configuration-coordinate diagram showing the total energy $\Sigma(Q)$ of the resonance state as a function of lattice distortion Q. The total energy is a minimum at $Q=Q_0$. It is a sum of the electronic energy and the lattice distortion energy which have competing dependences on lattice distortion. The lattice distortion energy $\frac{1}{2}\kappa Q^2$ is a quadratically increasing function of Q and it is indicated by the parabola passing through the undistorted resonance state at E_0. The electronic energy $E(Q)$ is a linearly decreasing function of energy and it lies within the band gap. Because the electronic state lies within the band gap, the resonance state becomes a real bound state with a corresponding lifetime.

$$E(Q_0)=E_0-2E_L \tag{3}$$

and the total energy

$$\Sigma(Q_0)=E_0-E_L. \tag{4}$$

In Fig. 1, the minimized total energy $\Sigma(Q_0)$ lies within the band states, but E_L is large enough that the electronic state at $E(Q_0)$ lies below the Fermi energy E_F. For this to occur, the lattice relaxation energy E_L must exceed the total energy relative to the Fermi energy, $\Sigma(Q_0)-E_\mathrm{F}$. If E_L is sufficiently large, then the apparent resonance state at energy $\Sigma(Q_0)$ is effectively an infinite-lifetime bound state because the electronic state lies below the Fermi energy.

Other effects on the lifetime of this resonance state can now be considered. The nonradiative and radiative transition rates can be analyzed by our considering transitions to the representative band state at $E=E_\mathrm{F}$. Nonradiative transitions involving multiple phonon emission are induced by nonadiabatic terms in the electron-lattice Hamiltonian, and the temperature dependence of this rate can be understood in terms of the energy barrier E_b at the crossing point Q_c shown in Fig. 1.[6] The rate is $1/\tau_\mathrm{nr}=(1/\tau_0)\exp(-E_b/kT)$ in which $1/\tau_0$ is the high-temperature prefactor and $E_b=(E_0-E_\mathrm{F}-2E_L)^2/4E_L$ is a "kinetic barrier" energy schematically indicated in Fig. 1 ($E_b\approx 100$–500 meV). This nonradiative rate becomes very small when $kT\ll E_b$. The radiative transition rate can also be analyzed with use of Fig. 1. Such transitions do not involve a change in configuration coordinate Q, and therefore a transition from the defect state to the band state must lie on the vertical line passing through $Q=Q_0$.[6] By inspection, the only possible transition involves absorption of photons. To summarize the analysis of the two transition mechanisms, this unusual resonance state will be long lived in the dark at low temperature.

In many cases, this analysis yields a result which can be obtained from the classic configuration-coordinate diagram shown in Fig. 1. From Eq. (3), we find that the resonance state can be long lived if $E_0-E_\mathrm{F}>2E_L$. From the definition of E_b, we observe that this is equivalent to $E_b>0$. The latter criterion can be tested by our simply inspecting a configuration-coordinate diagram while ignoring the concept of resonance states.

The simple configuration-coordinate analysis can often lead to erroneous conclusions. Thus the resonance-state concept is necessary in general. In many cases, the electronic state will rapidly "dephase" into band states which will reduce both the electron-lattice coupling and the relaxation energy to zero. The configuration-coordinate diagram will show a nonzero E_b but it will play no role in controlling the kinetics. Consider, for example, the case in which the localized-state spring constant κ is reduced such that $\kappa < \kappa_0$. Examining Fig. 1, one can envision reducing κ, the curvature of the parabolic energy surface, while maintaining the barrier E_b at a fixed value. The electronic resonance will lie within the band states when κ becomes sufficiently small. For this and smaller spring constants, the lifetime of the resonance state will be determined by the electronic dephasing rate rather than the kinetic rate. Other cases also require an analysis in terms of resonance states.[8]

The conditions needed to form long-lived resonance states can now be described before the application of this analysis to particular semiconductors.[8] The resonance state must be localized which requires that it be derived from a high-DOS band.[5,8] However, it must reside in a low-DOS band if it is to be narrow. This is the case for GaAs which has a small conduction-band-edge DOS $D(E) \propto m_\Gamma^{3/2} E^{1/2}$ corresponding to the small Γ-point effective mass $m_\Gamma \approx 0.067 m_0$. However, both the L and X points have much larger DOS because of the large masses ($m_L \approx 0.5 m_0$ and $m_X \approx 0.85 m_0$). Thus an L- and X-point-derived state appears "sharp" if it resides within the low DOS associated with the Γ point.

Such a resonance state can become a bound state in a semiconductor alloy such as $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$ because the character of the conduction-band edge changes from Γ-like to X-like at an alloy composition $x \approx 0.44$. As alloy composition or pressure varies, an s-like state localized by a central-cell potential should be "attached" to the center of the s-like spectral DOS of the four lowest conduction bands.[5] To a good approximation the L point defines the center of the s-like conduction-band DOS in AlGaAs.[5] Thus one expects that an s-like deep level will have the same composition dependence as the L point.[9]

We now consider the experimental observation of long-lived resonance states associated with the DX center in $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$. The original microscope model for the DX center is a donor-vacancy pair,[10] but recent work has suggested that the donor alone may cause the phenomenon.[4,11-15] Recent work showing sample-dependent deep-level transient spectra suggests that both the donor-vacancy and the substitutional-donor models are incomplete.[16] In the spirit of specificity and simplicity, however, we focus on substitutional Si donors in $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$. We emphasize that this analysis also applies to impurities in other semiconductors.

We assume a cation-site Si donor and compute the unrelaxed energy $E_0(x)$ using a tight-binding Green's-function method.[5,8] This energy is shown as a function of alloy composition in Fig. 2. Data points for the relaxed total energy $\Sigma(Q_0,x)$ are also shown in Fig. 2. The data were obtained by analysis of the Fermi-level dependence on doping concentration[3,17] for $x < 0.2$ and of Hall data[18,19] for $x > 0.2$. The resonance-state energies in GaAs are slightly dependent on doping concentration, a feature which has been interpreted as due to screening.[3] Only the lowest doping concentration datum point for GaAs is shown in Fig. 2 ($E_{\mathrm{Si}} = 174$ meV for $n_{\mathrm{Si}} = 4.6 \times 10^{18}\ \mathrm{cm}^{-3}$).[3] The band-structure variation is derived from recently reported data for Γ and L gap variation through the alloy system[20] and with the GaAs and AlAs X points shifted slightly upward while maintaining the conventional bowing parameter.[21]

The quantitative agreement is surprising when we consider the crudeness of the calculation which includes only the central-cell potential of the impurity.[5,8] Although the theoretical curve lies approximately 200 meV below the data points, the qualitative agreement is very good in that both the theory and the data have nearly the same composition dependence. Inclusion of static lattice relaxation would shift the theoretical levels upward by approximately 200 meV (see Ref. 13); this empirical contribution is omitted to avoid the impression of curve fitting.[8] Similar agreement between theory and data has been obtained in the application of this theory to anion-site N in GaAsP.[5]

In comparing the theory and the data, we now focus on the magnitude of the lattice relaxation energy E_L. The total energy $\Sigma(Q_0,x)$ seen in Fig. 2 is consistent with an s-like central-cell potential localized state whose energy E_0 is lowered by a small, composition-independent lattice relaxation energy E_L. The minimum lattice relaxation energy is determined by $\Sigma(Q_0,x)$ relative to the *Fermi energy* (not shown in Fig. 2). Thus, E_L

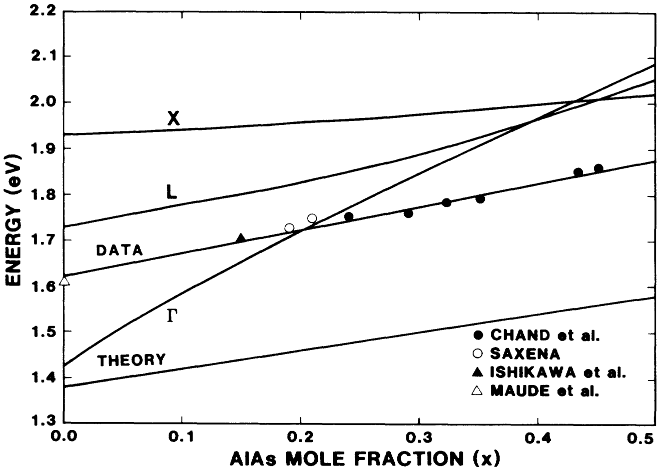

FIG. 2. The DX-center data [total energy $\Sigma(Q_0,x)$] and theory [electronic energy $E_0(x)$] as a function of alloy composition x for Si-doped $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. For all compositions, the relaxed electronic state $E(Q_0,x)$ lies below the Fermi energy (not shown). Thus this state is a long-lived resonance state for $x < 0.2$ and a bound state for $x > 0.2$.

must exceed $\Sigma(Q_0,0)-E_F \approx 50$ meV to explain GaAs data[3] and similarly $\Sigma(Q_0,0.15)-E_F \approx 50$ meV to explain the $Al_{0.15}Ga_{0.85}As$ data.[17] These energies are smaller than the deep-donor binding energy to the L point. Thus the magnitude of E_L is consistent with a small lattice relaxation model.[4,12-14] Turning to the large lattice relaxation model,[10] one can readily extend this model to include the resonance states discussed in this paper. In this model, $E_L \approx 750$ meV, and thus this model is also consistent with our analysis of the data.

An experiment to test the *DX* center models can be suggested. A hydrostatic pressure $P \approx 25$ kbar can be used to drive the GaAs *DX* center into the band gap.[11] For $Al_xGa_{1-x}As$, variation of pressure is roughly equivalent to variation of the alloy composition, and this pressure corresponds to $x \approx 0.3$. By cooling of the sample under pressure, the *DX* centers can be filled. The large lattice relaxation model predicts that the *DX* centers will remain occupied after the pressure is released at low temperatures. However, if E_L is small as predicted by the small lattice relaxation model,[4] this state will be very sensitive to the position of the Fermi level. Thus for a lightly doped sample, the resonance state will rapidly dephase into band states.

In summary, a new class of long-lived resonance states has been predicted in this paper. These states explain recent data which have been interpreted in terms of long-lived resonance states associated with the *DX*-center model. These states are consistent with both small and large lattice relaxation models for the *DX* center.

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